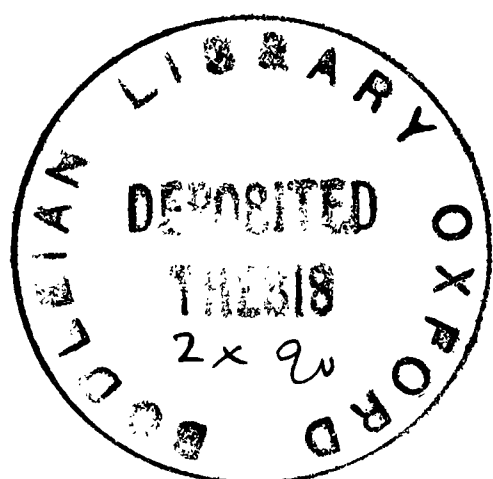


ELECTRON-LATTICE COUPLING IN CONJUGATED POLYMERS

A thesis submitted for the degree of Doctor of Philosophy at the
University of Oxford



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ABSTRACT

The possibility of a number of applications has fuelled the study of conjugated polymers for some years. Because of the level of electron-lattice coupling in these materials, it is necessary to perform self-consistent calculations of electronic wave functions and atomic positions in order properly to study the defects responsible for their behaviour.

Early empirical methods for performing such self-consistent calculations have proved remarkably successful in many of their predictions, but have still displayed certain shortcomings, primarily due to their failure satisfactorily to treat electron-electron interaction. They are still useful in a number of cases, however, and have been used here to derive some results which have not been obtained elsewhere, or which have only been derived in a more time-consuming manner than is necessary.

This thesis is primarily concerned, though, with the development of a method which enables semi-empirical Hartree-Fock theory to be used in a self-consistent manner. The method is novel in that it performs the atomic relaxation and wave function calculation simultaneously and requires no numerical derivatives to be calculated. Both of these features lead to a method that is extremely efficient in terms of computer time and which can therefore reasonably be applied to molecules sufficiently large to model conjugated polymers.

The results obtained by this new method are shown to be able to account for most of the shortcomings of the earlier methods, in particular their failure satisfactorily to explain the quenching of luminescence in cis-polyacetylene and their poor predictions of the relative strengths of the two photoinduced absorption peaks in polythiophene. The ability of trans-polyacetylene (t-PA) to support a novel type of dynamic defect known as a breather is also verified. A quantitative estimate is made of the

mobility of the fundamental defect in t-PA, known as a soliton, and this is in good agreement with experiment.

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1.1 INTRODUCTION

Most conjugated polymers behave as strongly anisotropic (i.e. approximately one-dimensional) semiconductors, with band gaps typically in the range 1.4-3.0eV. Whereas in traditional (three-dimensional) semiconductors, the charge carriers are free electrons and holes, with energies close to the band edges, conduction in conjugated polymers is believed to be mediated by charged defects, which are the species formed on doping (the electron-lattice coupling is sufficient to create localised, polaronic states). At low dopant levels, conductivity appears to be due to the mobility of these defects themselves along a chain; at higher concentrations, various more complicated mechanisms, involving hopping between chains or between defects as the conductivity-limiting process, have been proposed (and reviewed by Kivelson (1986)). The possibility of a number of applications has fuelled the study of these defect states: the doping process in a number of polymers can be carried out electrochemically and reversibly (Chung *et al.* 1984, and numerous others), leading to applications as electrodes in lightweight rechargeable batteries, and doped polymers can be incorporated into cloths to provide anti-static materials (Gregory *et al.* 1989). The conductivities attainable by doping can be as high as that of copper (Basescu *et al.* 1987), and the consequent conductivity:mass ratio (which is an important quantity when considering applications in the aerospace industries, for example) substantially higher than that of any metal.

In the past, a number of semi-empirical methods have been used to investigate these defect states, ranging from the phenomenological Hückel-type theory of Su, Schrieffer and Heeger (SSH) (1980), which has a continuum approximation due to Takayama, Lin-Liu and Maki (TLM) (1980) which is exactly soluble in certain simple cases, to long-established

quantum chemical techniques based on Hartree-Fock theory, such as MNDO (Stafström and Brédas 1988). The predictions of the SSH model, especially in the TLM approximation, have been reviewed by Heeger *et al.* (1988). Owing to the level of electron-lattice coupling in these materials, it is necessary, when calculating defect properties, to perform calculations which treat the atomic displacements self-consistently with the electronic wave function calculations, and in this thesis the self-consistency process has been applied both to the SSH model and to semi-empirical Hartree-Fock theory, using a method based on its molecular dynamical application in the CNDO and INDO parametrisations. The results of each set of calculations are summarised below, so far as is necessary to illustrate the various defect types that may be formed in conjugated polymers; a more detailed outline of the methods used, and of the results obtained, forms the body of this thesis.

1.2 CONJUGATED POLYMERS

The archetypal example of a conjugated polymer is trans-polyacetylene (t-PA), whose structure is shown in fig. 1.1. The carbon atoms are sp^2 -hybridised, with one p_z (π) electron per carbon atom not being included in the σ -bond backbone (taking the plane of the polymer to be the x-y plane).

In simple Hückel theory, these electrons would be expected to form a band of width $4t_0$, where t_0 is the hopping integral $\langle n|H|n+1 \rangle$ between adjacent carbon atoms. This band would be half-filled and thus t-PA would behave as a one-dimensional metal.

The reason why this does not occur is characteristic of all one-dimensional metals: a Peierls distortion occurs (Peierls 1955), doubling the size of the unit cell and introducing a band gap in the middle of the band. This was first proposed for t-PA by Longuet-Higgins and Salem (1959); in chemical terms, the backbone consists of alternating single and double

bonds (although the bonds are actually rather more similar in terms of length and of bond order than is implied by this representation, it does form a useful basis from which to discuss the behaviour of the system). If we use some parameter u_0 to represent the amplitude of the Peierls distortion, it is easily shown that the cost of this distortion, in terms of the energy needed to distort the σ -bond backbone, is $O(u_0^2)$, while the gain in electronic energy is $O(u_0)$. A graph of total energy against u_0 is shown in fig. 1.2. Note that there are two equal minima, corresponding to positive and negative u_0 ; the two degenerate states are labelled A and B in fig. 1.3 and are clearly related by symmetry.

1.3 SOLITONS AND THE DIMERISATION PARAMETER

In order properly to study the distortion around a defect in a polymer chain, it is helpful to define some quantity which:

- (i) is constant in the ground state,
- (ii) directly represents the degree of dimerisation, and
- (iii) varies smoothly along the chain even in the presence of a defect or defects.

The method used here is very simple, although not unique. The simplest quantity that can represent the degree of dimerisation of a polymer is the difference between adjacent bond lengths, but since the ground state bond lengths alternate along the chain, the difference between adjacent bond lengths, although constant in magnitude, will alternate in sign. If we multiply this difference by a factor $(-1)^n$, however, the result will be a representation of the degree of dimerisation which is constant in the ground state as required. The *dimerisation parameter* is thus defined by:

$$d_n = (-1)^n(b_{n,n+1} - b_{n-1,n})$$

where $b_{n,n+1}$ is the length of the bond joining atoms n and $n+1$. The degree of dimerisation actually increases slightly towards the ends of a polymer chain, but this effect is neglected for the purposes of this discussion.

Note that states A and B of fig. 1.3 correspond to dimerisation parameters of different sign, since in state A the bonds corresponding to n even are the short bonds, while in state B it is those corresponding to n odd that are shorter.

Now we can consider the basic defect in t-PA. Imagine that we constrain one end of a polymer chain to be in state A and the other to remain in state B (how this may be done is outlined below). The simplest model of the intervening (defect) region is that of fig. 1.4, where the transition from A-state to B-state is abrupt, and there is an unpaired electron (free radical) completely localised on the central carbon atom. In fact, the change in dimerisation parameter is more extended; in the TLM approximation, the dimerisation parameter is proportional to $\tanh(x/\ell)$, where the half-width ℓ is approximately 7 C-C spacings, and the wave function associated with the defect extends over a similar range. Conditions of bonding (from the chemical viewpoint) or orthogonality between wave functions (in the quantum mechanical framework) dictate that there remain one localised state, and (within the Huckel approximation) this state has energy at midgap.

This type of defect, whose existence was originally proposed by Longuet-Higgins and Salem (1959), and which was first considered in a quantitative manner (albeit in a very simple form) by Pople and Walmsley (1962) is known as a *soliton* (originally *kink soliton* or *bond-alternation defect*), in view of its obvious non-linearity and of the similarity of the TLM continuum model to more familiar equations of field theory, which display more traditional solitonic solutions. In addition, the soliton's large size means that it can move freely along a chain without changing its shape; this is another important characteristic of all types of solitons, and one first noted by Russell (1844).

TOPOLOGICAL RESTRICTIONS: SPIN AND CHARGE. The spin-charge relations of a soliton are slightly unusual: in the neutral chain it is associated with

an unpaired electron and thus has spin $S=\frac{1}{2}$; this electron can be removed, or another electron added, to give defects with spin $S=0$ and charge $\pm e$. The reason why these relations do not violate Kramers' theorem, and the means by which we were able to enforce the change from A state to B state above, are closely allied and are illustrated in fig. 1.5. A defect-free chain with an even number of carbon atoms is terminated by a "double" (i.e. short) bond at each end; if we attempt to create just one soliton, one end of the chain is forced to end with a "single" bond, thereby leading to a second unpaired electron, this one on the final carbon atom (just as in the discussion of the soliton, this electron will not be associated entirely with this one carbon atom, but its wave function will extend into the chain over a few carbon atoms, and the distortion will rather resemble that of half a soliton). We cannot create just one localised state, but we must create them in pairs.

If, instead of an "even" chain, we consider a uniformly dimerised chain with an odd number of carbon atoms, and no defects, the bonding pattern dictates that it is forced to end with a single bond and an unpaired electron; this state is free to move up the chain, but cannot vanish entirely, since the chain must either contain a reversal in its dimerisation (i.e. a soliton) or end with a single bond (fig. 1.5 again). Since the total number of p_z electrons in the chain is odd (and all the other electrons are paired), the necessary existence of a single localised state is to be expected.

In practice, any localised state created at the end of a chain will move into the chain's interior, in order to maximise the reduction in σ -bond energy associated with the defect, and will become another soliton (this was first predicted within a dynamical simulation by Su and Schrieffer (1980), and has been verified within the CNDO method (see §6.7), as well as for the SSH model). It is one of the properties of a soliton (in mathematical terms) that any distortion, injected at one end of an infinite

system, will resolve itself into a number of solitons by the time it reaches the other end, and an echo of this property can be seen in these simulations, with the distortion changing shape and beginning to resemble a soliton as it moves up the chain.

1.4 GENERAL (NON-DEGENERATE) POLYMERS

Trans-polyacetylene is, however, not a typical conjugated polymer: the degeneracy between A and B states makes it a very special case (although a few other polymers which display an equivalent degeneracy can be found, they have much larger repeat units and the concept of an extended defect becomes somewhat tenuous). Other polymers, such as cis-polyacetylene (c-PA) and polypyrrole (PPy) are more typical; in fig. 1.6 they are drawn in their stable forms, the *cis-transoid* and *trans-cisoid* isomers respectively (if we were to define a parameter u_0 to represent the amplitude of the Peierls distortion as for t-PA above, then one of these polymers would have a ground state corresponding to positive u_0 and the other to negative u_0 ; graphs of total energy against u_0 , analogous to fig. 1.2, are shown in fig. 1.7). The reasons why these particular isomers are stable is not difficult to see: in c-PA, steric repulsion between neighbouring hydrogens is reduced in the *cis-transoid* isomer, while in PPy it is the fact that the C-N bond length necessary to complete the heterocycle is smaller in the *trans-cisoid* isomer than in the *cis-transoid* isomer that leads to the stability of this form.

It is immediately clear, therefore, that solitons cannot exist in c-PA or PPy, since their existence implies extended regions of both A and B states. Any defect that occurs in these polymers must be bounded by the same dimerisation state at each side, rather than interpolate between two different states (see fig. 1.8). It is not so easy to represent this form of defect in chemical bonding terms as the soliton, since the actual amount by which the chain is distorted is no longer dictated by the topology of

the defect, but two possible representations are shown in fig. 1.9, using c-PA as an example. The first represents a minimum dimerisation of zero, the second has a "negative" dimerisation in the centre of the defect, corresponding to a region of the unstable trans-cisoid isomer. This form of defect is associated with a pair of localised states, which are (within the SSH model) symmetrically located about midgap, within the band gap (the precise position of the states within the band gap depends on the geometry of the defect: a very shallow distortion of the lattice will only move the states out of their respective bands by a small amount, while at the opposite extreme the defect will split into a pair of solitons and the states will meet at midgap). Clearly, this type of defect will not be stable in an uncharged, unexcited singlet state, as it will decay trivially into the ground state, but addition of a single charge to the system will leave no such decay route available and will stabilise the defect.

As for the soliton, the defect will in reality be substantially more extended than implied by fig. 1.9. Its form is entirely analogous to that of a polaron in more familiar materials such as the III-V semiconductors or the alkali halides, in that it consists of a localised charge coupled to the longitudinal optic modes (i.e. the dimerisation) of the host. Sometimes, this class of defect in conjugated polymers is known as a *polaron soliton*, but there seems no reason for qualifying the description and it is now more generally known as a polaron wherever it occurs. The charge:spin relationship of a polaron is more traditional than that of a soliton: polarons carry both charge and spin.

Since the defect of fig. 1.9 has two unpaired electrons, we are of course free to remove them both, rather than just one, leading to a doubly charged state of spin zero (alternatively, we could pair up both electrons by adding two more). If the result is stable with respect to decay into two polarons, we have a *negative U* effect (Anderson 1975, Street and Mott 1975), and the resulting defect is known as a *bipolaron* (in the case of

t-PA, stability with respect to two-soliton decay also needs to be considered, but it should be understood that this is a distinct process from the two-polaron decay described by the negative U effect).

1.5 QUANTITATIVE STUDY OF DEFECT FORMATION

We can now start to investigate quantitatively the energies of each of the defects we have been considering. The SSH model provides an easily comprehensible framework, although results from CNDO will be introduced on occasions as they are more likely to be reliable. The SSH model, as originally proposed, does not consider electron-electron interaction in any form, for example, and even the more commonly used empirical corrections to the model fail to do so in any reliable manner, so the question of the negative-U effect is best handled by CNDO.

SINGLE CARRIERS IN t-PA: ENTHALPY OF SOLITON FORMATION. Consider t-PA first, and assume that we are dealing with a chain of even length (to make the boundary conditions as simple as possible). The band gap is approximately 1.4eV, and so (taking the centre of the gap, i.e. the localised p_z -orbital energy, as the zero of energy), the electronic energy required to create a soliton is 0.7eV, since one electron must be raised from the valence band edge to midgap. The positive, quadratic contribution to the chain energy that arose (see §1.2) because dimerisation distorted the σ -bond system is reduced around a soliton, though, and there is a gain of approximately 0.25eV from this source. Thus the total cost of creating a soliton in a t-PA chain is about 0.45eV (the exact analytic result from calculations within the TLM model is E_g/π , where E_g is the band gap). Including electron-electron interaction in the simplest manner possible, i.e. via an on-site Hubbard U, increases the energy of a charged soliton by ≈ 0.11 eV, a value derived indirectly from the results of photoinduced absorption on t-PA by Blanchet *et al.* (1983) (see §§3.6 and 3.7 for details). The energy of an uncharged soliton is decreased by the same

amount, so charged and uncharged solitons have energies of approximately 0.56eV and 0.34eV respectively within this model. It should be remembered that topological considerations prevent us from creating just one soliton, so these energies should be understood to represent half of the energies required to create soliton pairs.

ENTHALPY OF POLARON FORMATION. The alternative way to remove an electron from the chain is via polaron formation. The gain in energy, due to the localised reduction in dimerisation amplitude, is strongly dependent on the depth of the distortion, as is the loss of energy due to the creation of the localised electronic states, and this is why self-consistent calculations are necessary to study the defects in conjugated polymers with any accuracy. Analytic solution of the TLM model yields localised states at $\pm E_p = E_g/2$ (Fesser *et al.* 1983), while numerical self-consistent solution of the SSH model gives states slightly closer to the centre of the band gap, with $E_p = 0.48\text{eV} = 0.69E_g/2$. The consequent lattice distortion is fairly slight, but extends over a slightly larger region than that of a soliton, and leads to a gain in energy of $E_{\text{relax}} = 0.29\text{eV}$. Thus the energy required to form a charged polaron is:

$$\begin{aligned} E_{\text{pol}} &= E_g/2 + (E_g/2 - E_p) - E_{\text{relax}} \\ &= 0.63\text{eV}, \end{aligned}$$

representing a saving of 0.07eV over the simple removal of an electron from the valence band without lattice distortion. CNDO predicts a slightly greater lattice distortion than SSH, but the results are qualitatively similar. Inclusion of a Hubbard U into the SSH model has no effect on the polaron energy, for reasons that will be discussed in §3.6.

Given the energies required to form charged solitons and charged polarons in t-PA, it is clear that solitons will be formed preferentially. Polarons will still be formed, of course, where boundary conditions prohibit soliton formation (e.g. on adding a single charge to a chain of even length), since the energy required to create a pair of solitons, one charged and one

uncharged (which is the only way to store a single charge between solitons within these boundary conditions) is 0.9eV.

NON-DEGENERATE POLYMERS. Singly charging a chain of a polymer without ground state degeneracy leads to a similar situation in respect of the polaron creation energy; by modifying the SSH model to represent c-PA (see §2.4), we obtain new values:

$$E_g=1.94\text{eV} \quad E_p=0.77\text{eV} \quad E_{\text{relax}}=0.28\text{eV},$$

and hence $E_{p01}=0.89\text{eV}$, a saving of 0.08eV on the direct removal of an electron from the valence band. Again, CNDO predicts a slightly greater lattice distortion, presumably because it takes into account the repulsion of the now positively-charged carbon atoms and aims to spread the defect out further as a result.

PAIRS OF CARRIERS. The situation becomes more interesting when a second charge is added. Again, we deal with t-PA first. Both sets of self-consistent calculations agree that the charged bipolaron in t-PA is unstable with respect to decay into two solitons; we cannot calculate the energy of a bipolaron as such, since the geometry relaxation routines will simply lead to this decay (note that the energy required to add the second charge is, in the SSH model, rather less than that required to add the first, since the first charge will form a polaron, of energy 0.63eV, and the second will convert this into a soliton pair, of energy 1.12eV when the Coulomb energies of the solitons are taken into account. This neglects Coulomb interaction *between* the solitons, of course, but since the solitons are free to separate this should not, in principle, affect this argument). Now consider c-PA, where the two-soliton route for bipolaron instability is forbidden. Within SSH, the energy saving due to the σ -bond distortion is 0.43eV, and the new states are at $\pm 0.45\text{eV}$ (as expected, they are closer to the band centre than the states due to the single polaron, as the lattice distortion is greater, but in the bipolaron case the energy of these states is actually immaterial, since they will be empty). Thus the total energy

required to form a bipolaron is $E_{\text{bip}} = E_g - E_{\text{relax}} = 1.51\text{eV}$, a saving of 0.27eV on the formation of a pair of polarons.

It is not surprising that bipolarons are predicted to be stable in the SSH model, since electron-electron interaction is not considered and the main term acting to destabilise the bipolaron is therefore ignored. Adding an on-site Hubbard U term to the SSH model gives a Coulomb energy of about 0.25eV for the bipolaron, a figure, like its equivalent in t-PA, derived indirectly from the results of photoinduced absorption, in this case on polythiophene by Vardeny *et al.* (1986). However, the uncertainty in this figure is substantial and the evidence for the stability, or otherwise, of bipolarons in the SSH model should not be regarded as conclusive.

The results of CNDO calculations on c-PA should be more reliable, however, since electron-electron interaction is considered in a self-consistent manner. We find that the energy of a polaron in a chain of length 32 (i.e. a molecule of $\text{C}_{32}\text{H}_{34}$) is -0.60eV (we are no longer free to choose our zero of energy to lie in midgap, so this value is quoted relative to the energy required to remove an electron at fixed geometry), while the equivalent bipolaron energy is -3.11eV (these are figures for positively charged defects), making the bipolaron substantially more stable than a polaron pair. The energies of the various charged defects in c-PA are summarised below, relative to the energies required to charge the chain at fixed geometry.

Table 1.1 Defect energies in c-PA (in eV)

	SSH	SSH with Hubbard U	CNDO
Polaron	-0.08	-0.08	-0.60
Bipolaron	-0.43	-0.18(?)	-3.11

These results are in good agreement with the experimental evidence that bipolarons are the species formed on doping at moderate to high

concentrations (this evidence will be discussed below). At lower concentrations, polarons should still be observed under normal conditions, owing to the significant barrier to polaron recombination (the Coulomb repulsion of a polaron pair is a much longer-range effect than their mutual attraction due to the lattice distortion); a graph representing how the energy of a pair of polarons depends on their separation is shown in fig. 1.10. Crude numerical estimates of the barrier height (modelling the polaron charge density by a Gaussian distribution, and the Coulomb integral by a term proportional to $1/\sqrt{R^2+a^2}$, with a about 2 lattice spacings) lead to values of the order of 1eV; the situation is complicated by the presence of the (charged) dopant ions, however.

1.6 EXPERIMENTAL EVIDENCE CONCERNING DEFECT TYPES

Evidence for the nature of the defects formed on doping conjugated polymers has been obtained from ESR measurements, relying on the different charge:spin relationships of the various defects discussed above. Ikehata *et al.* (1980) measured the magnetic susceptibility of t-PA as a function of dopant level, up to 13.8% doping (expressed as the ratio of dopant molecules to carbon atoms). They found that t-PA exhibited a small Curie susceptibility in the undoped state (about 4×10^{-4} spins per carbon atom), which they attributed to the presence of a small number of neutral solitons (presumably imposed by the boundary conditions, since the energy required to create a soliton pair is sufficiently large that thermally-created solitons should not exist in appreciable quantities). On doping, the spin concentration *decreased*, corresponding to the ionisation of these solitons (recall that charged solitons are spinless), and no Curie susceptibility is seen at higher dopant concentrations than about 2-3%. Above about 7%, a significant Pauli contribution to the susceptibility is seen, representing an effective semiconductor-metal transition.

Similar experiments have been performed on PPy (Scott *et al.* 1983) and the

susceptibility is observed to increase initially, until at about 1% doping it reaches a maximum and starts to tail off. This is consistent with the formation of polarons initially, to be replaced by bipolarons at higher dopant levels as the polarons combine. Chen and Heeger (1986) performed the same experiment on polythiophene, but at each doping level measured how the susceptibility varied with time. They found that, even when significant susceptibility (and hence appreciable polaron concentration) was initially observed, it would decline to a very small value after a few days, as the polarons overcame the kinetic barrier to recombination. The time scale over which this process will occur will presumably depend on the precise polymer under consideration and on the sample temperature, and results akin to those of Scott *et al.* would be expected whenever such an experiment is carried out at low temperature or over a time scale smaller than the characteristic polaron-bipolaron conversion time (which will chiefly depend on the barrier height of fig. 1.10). Simple numerical models of this competitive polaron-bipolaron formation are easy to write, and yield results in good qualitative agreement with the experimental data.

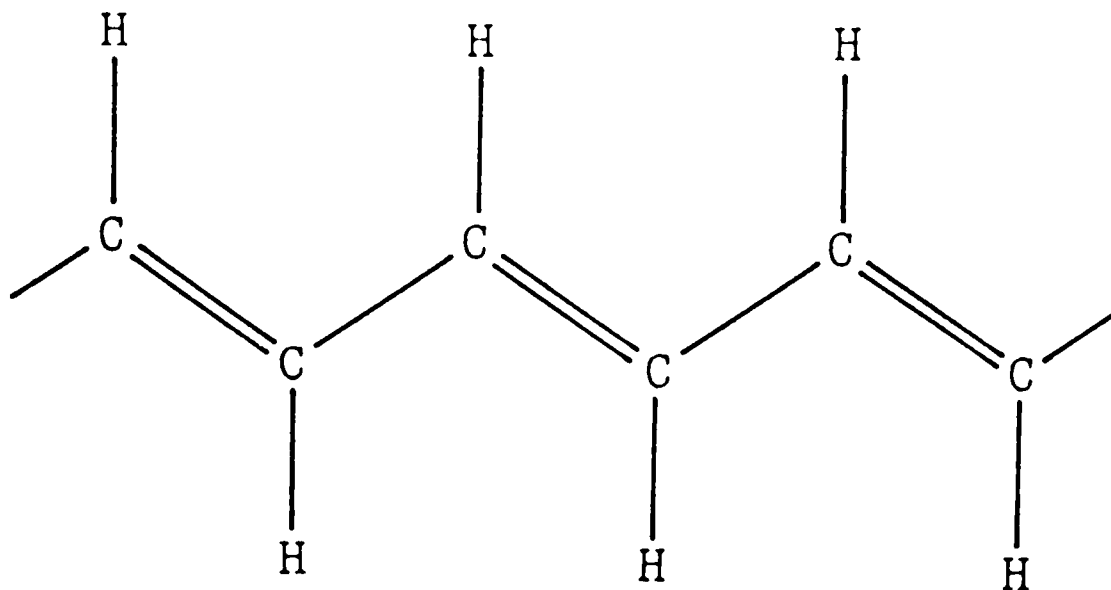


Fig. 1.1 Structure of trans-polyacetylene (t-PA)

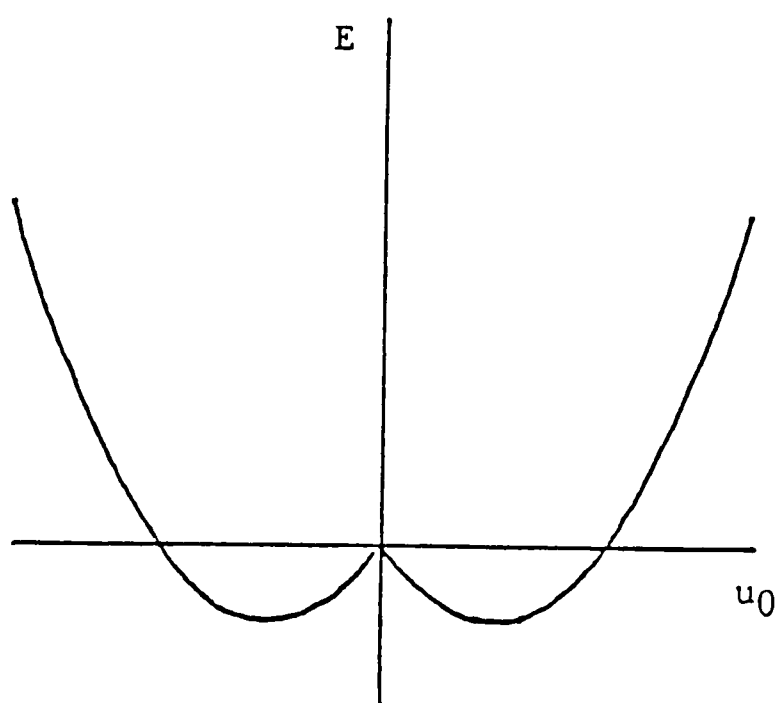


Fig. 1.2 Total energy E of a chain of t-PA, in terms of the degree of dimerisation u_0 . There is a positive quadratic term due to the distortion of the σ -bond system, and a negative term, linear in $|u_0|$, due to the gain in electronic energy on dimerisation.



A state



B state

Fig. 1.3 Degenerate ground states of t-PA. The two states correspond to the two degenerate minima of fig. 1.2.

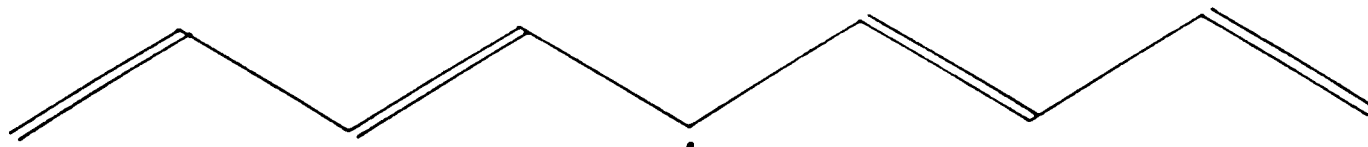


Fig. 1.4 Schematic representation of a neutral soliton in t-PA (see §1.3).

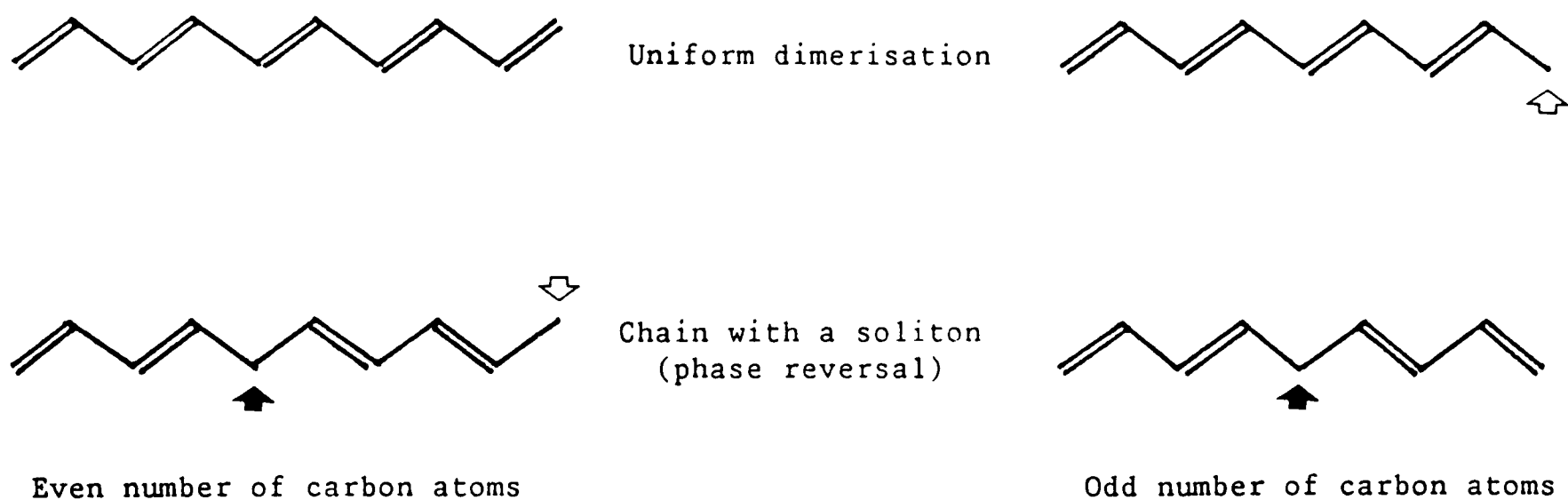


Fig. 1.5 Demonstration that the number of localised states in a chain of t-PA is fixed in parity. Adding just one soliton (phase reversal, full arrow) to an even chain leads to the formation of a single bond at one end of the chain (open arrow); with this there will be associated a second localised state. Similarly, adding a soliton to a uniformly dimerised odd chain has the effect of moving the localised state initially associated with the single bond at the end of the chain (open arrow) into the chain interior.

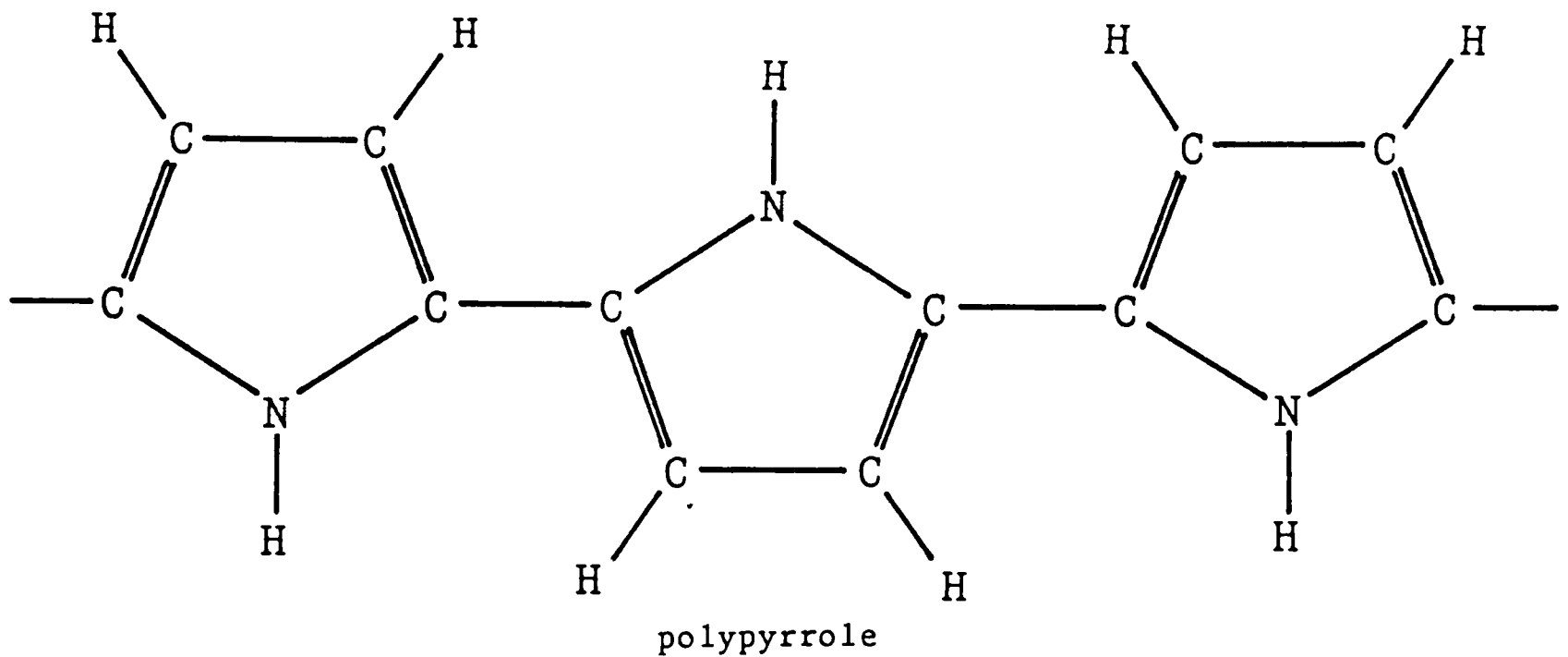
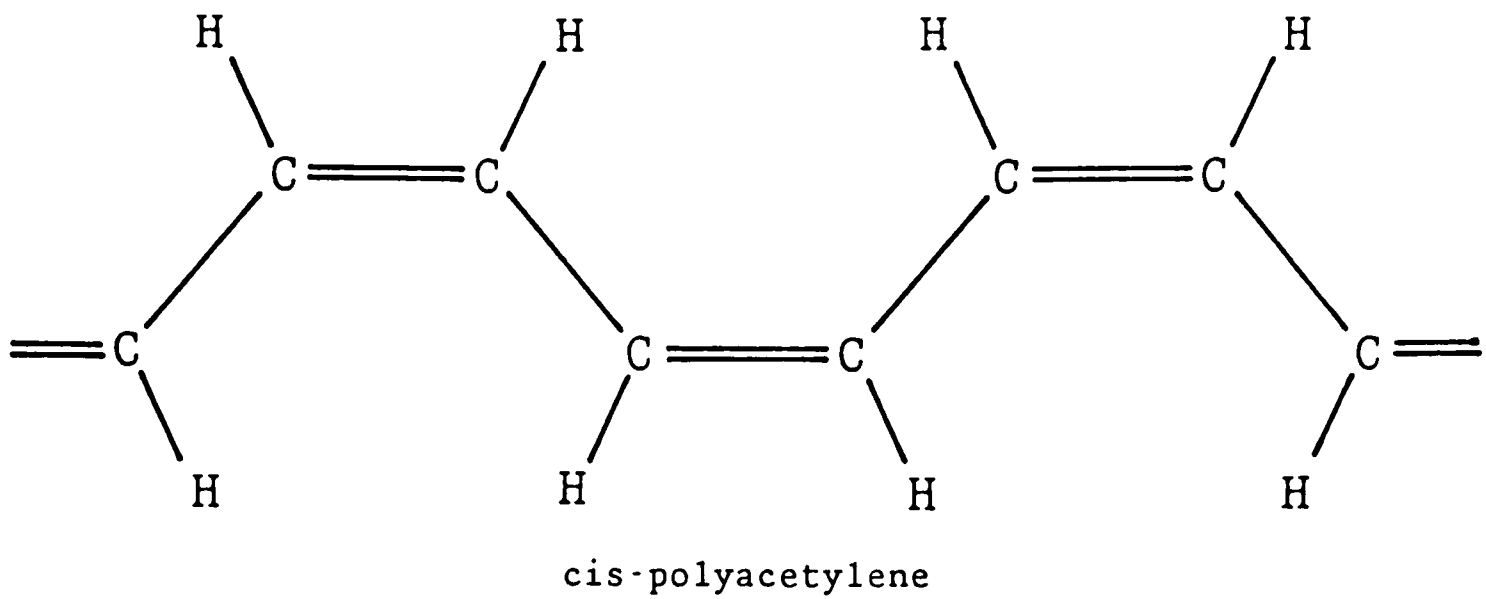


Fig. 1.6 Ground states of cis-polyacetylene (c-PA) and polypyrrole (PPy). The ground states are respectively the *cis-transoid* and *trans-cisoid* isomers.

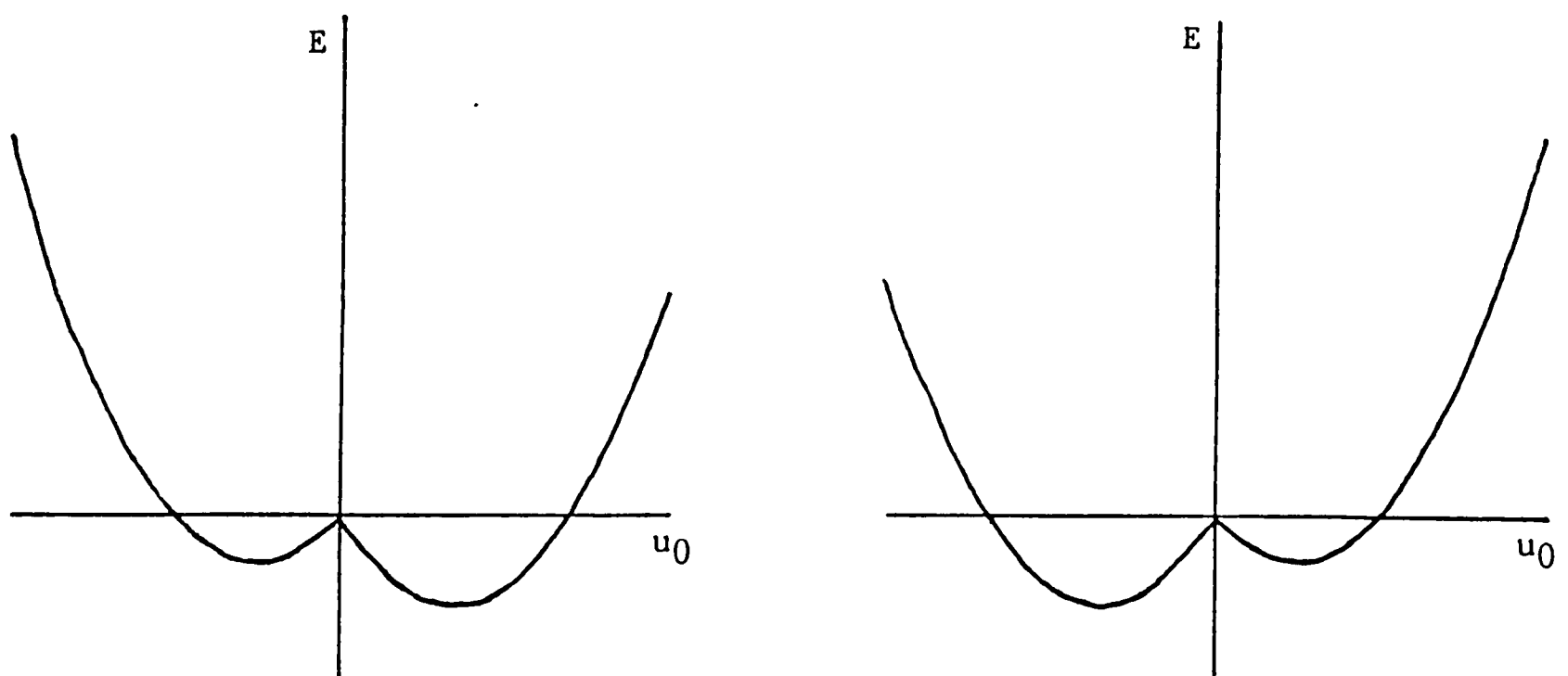


Fig. 1.7 Energy against dimerisation for non-degenerate polymers. The two states represented by positive and negative u_0 , which in c-PA would be the *cis-transoid* and *trans-cisoid* isomers, are no longer related by symmetry, for them to be degenerate.

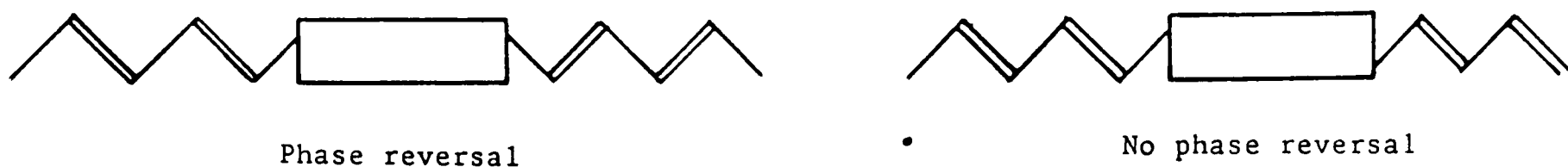


Fig. 1.8 t-PA can display two topologically inequivalent types of defect: those associated with a phase reversal from A state to B state or vice versa (*solitonic* defects) and those bounded by the same state at each end (*polaronic* defects). In the non-degenerate polymers such as c-PA and PPy, only polaronic defects can occur, since only one of the two dimerisation states is stable.

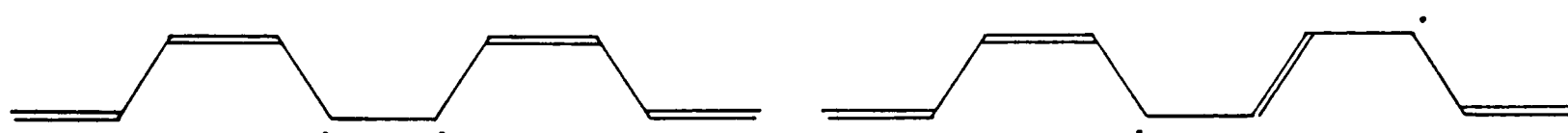


Fig. 1.9 Two possible representations of an uncharged polaronic defect in c-PA. The first form represents a local breakdown of the dimerisation, while the second could be regarded as a soliton pair, bounded due to the instability of the trans-cisoid isomer. Either or both unpaired electrons could be removed, in order to stabilise the defect.

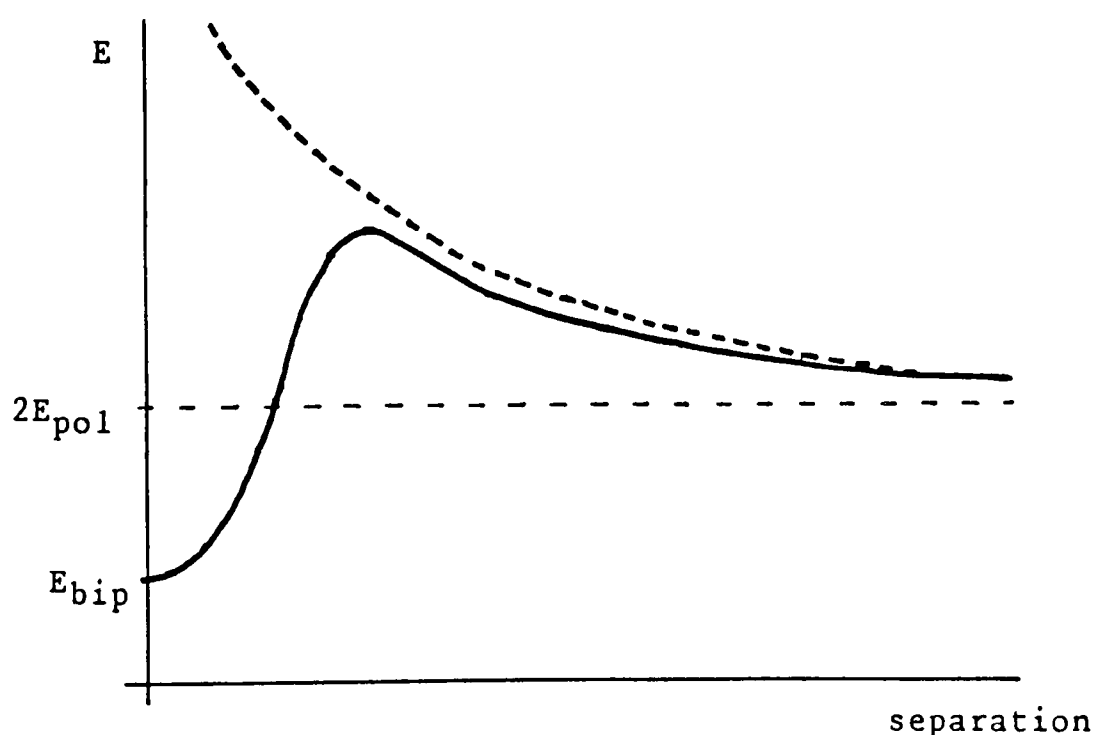


Fig. 1.10 Energy of a pair of like-charged polarons, as a function of their separation. The total energy has two main components: a short-range attractive part, caused by the interaction between the two lattice distortion patterns, and the (long-range) Coulomb term. The dashed curve plots this Coulomb repulsion in the long-distance limit, with $E \propto 1/R$. In this case, the short-range term is sufficient that the energy of a bipolaron is less than that of an isolated polaron pair; this is an example of the *negative U* effect (see p. 1.7).

2.1 INTRODUCTION

Su, Schrieffer and Heeger (SSH) (1980) modelled a chain of trans-polyacetylene (t-PA) as purely one-dimensional, with a co-ordinate system such that the displacement of the n 'th carbon atom from its place in the undimerised chain was u_n . The only energy terms they considered were a simple quadratic term in the bond lengths, representing the energy due to distortion of the σ -bond backbone, and the hopping integral between adjacent carbon atoms; this, in turn, they expanded linearly about its equilibrium (undimerised) value t_0 . Only the p_z (π) orbitals were considered, it being argued that the σ (bonding) and σ^* (antibonding) bands would lie well outside the π and π^* bands which would comprise the region of interest. Hence (using c_{ns}^+ and c_{ns} to represent creation and annihilation operators for p_z electrons of spin s at site n) they obtained the Hamiltonian:

$$H = - \sum_{ns} (t_0 - \alpha(u_{n+1} - u_n)) [c_{ns}^+ c_{n+1,s} + c_{n+1,s}^+ c_{ns}] + \frac{1}{2} K \sum_n (u_{n+1} - u_n)^2$$

When performing self-consistent relaxation calculations, it is necessary to add a constant C to the "bond length" $(u_{n+1} - u_n)$ that appears in the quadratic term, as otherwise the chain is unstable with respect to overall contraction (the overlap integral, and hence the electronic energy, decreases linearly with $(u_{n+1} - u_n)$, while the potential energy of the σ -bonds increases only quadratically).

This constant is chosen by implementation of the condition $u_{n+2} = u_n$ for all n in the ground state. For an undimerised chain, it is easily shown that this requires $C = -4\alpha/K\pi$; for a dimerised chain of t-PA we find $C = -1.250\alpha/K$, which value is derived in §3.4.

As explained in chapter 1, the undimerised chain is unstable with respect to a Peierls distortion, and the ground state has displacements given by $u_n = (-1)^n u_0$, where u_0 is a constant depending on t_0 , α and K (albeit not in

an easily quantifiable manner). t-PA has the property that ground states corresponding to positive and negative u_0 are degenerate (see chapter 1), but this is not true of more general polymers such as cis-polyacetylene (c-PA), polythiophene (PT) or polypyrrole (PPy). In order to model these more general polymers, it is necessary to add another term to the Hamiltonian, and the method used here is to add a term in the energy proportional to $\tilde{u}_n \equiv (-1)^n u_n$ (other authors, such as Fesser *et al.* (1983), add a term to the staggered displacement $\tilde{u}_n$ directly; these two methods are equivalent, as will be shown in §3.5). This leads to a modified SSH Hamiltonian:

$$\begin{aligned}
 H = & - \sum_{ns} (t_0 - \alpha(u_{n+1} - u_n)) [c_{ns}^+ c_{n+1,s} + c_{n+1,s}^+ c_{ns}] + \frac{1}{2} K \sum_n (u_{n+1} - u_n + C)^2 \\
 & + S \sum_n (-1)^n u_n
 \end{aligned} \tag{2.1}$$

The parameters that need to be determined are t_0 , α , K and S . We assume that the first three are independent of the polymer under consideration, since they are principally concerned with the behaviour of the carbon backbone, and choose them to fit the available data on t-PA. K is chosen to be $42 \text{ eV \AA}^{-2}$, a standard value given by Ooshika (1957) and Schugerl and Kuzmany (1981), although SSH chose a value of half this; t_0 is chosen to fix the total bandwidth $4t_0$ at its experimental value of 10 eV (Grant and Batra 1979), giving $t_0 = 2.5 \text{ eV}$, and α is chosen such that the band gap $8\alpha u_0$ is equal to its observed value of 1.4 eV (with u_0 fixed by the choice of t_0 , α and K). The resulting value of α is $6.1 \text{ eV \AA}^{-1}$, although SSH obtain $4.1 \text{ eV \AA}^{-1}$ due to their smaller value of K , and the dimerisation amplitude u_0 that results is $0.03 \text{ \AA}$ ($0.04 \text{ \AA}$ for SSH). The dimerisation amplitude can be compared against experiment; long and short bonds will differ in length by $2u_0/3$ (due to the geometry of the system, which is shown in fig. 1.1), and this difference has been measured to be $0.10 \pm 0.01 \text{ \AA}$ (Yannoni and Clarke 1983), in good agreement with the predicted value (rather less good agreement with that of SSH).

The mean bond length in t-PA is taken to be the length of the conjugated C-C bond in benzene, i.e. $1.40\text{\AA}$, and this leads to a C-C spacing along the chain of $1.22\text{\AA}$; this is redefined as the unit of length L for simplicity.

At this stage it should be noted that the values above are actually rather poor, for the simple reason that the experimental results to which they were fitted were fairly approximate. The nature of the original paper by SSH was such that its qualitative predictions were much more important than any quantitative values derived therefrom, and it was not crucial to fit the parameters too exactly; in fact, the band gap of t-PA may be as high as 1.7eV (the absorption tail starts at about 1.4eV , but this has been explained as being due to the existence of localised states, due to what is effectively the zero point motion of the lattice (Phillpot *et al.* 1989)), and the total bandwidth in t-PA is nearly 12eV . However, in order to compare the results of this thesis with those of other authors, the commonly accepted values of band gap and bandwidth are used here.

c-PA is used as an example of a polymer without a degenerate ground state; the final adjustable parameter S is chosen to fit the observed band gap of 2.0eV , and the value used to do this is $S=1.0\text{eV}L^{-1}$; smaller values of S have been used to examine trends on changing the degree of non-degeneracy of the polymer under consideration.

2.2 SELF-CONSISTENT SOLUTION OF THE SSH HAMILTONIAN

The self-consistent solution of the modified SSH Hamiltonian (2.1) is a two-step recursive process. Firstly, the Hamiltonian matrix is diagonalised for fixed values of the atomic displacements $\{u_n\}$; then the conditions that $\partial E/\partial u_n=0$ for all n are used to generate new displacements. How this is done is based on the method of Stafström and Chao (1984a), and summarised here. Stafström and Chao could only consider t-PA within their model, but the method has been extended in this thesis to allow for the treatment of non-degenerate polymers.

Expand the eigenfunctions (expressed in terms of their creation and annihilation operators $c_k^\dagger$ and c_k) over the atomic p_z orbitals by writing:

$$c_k^\dagger = \sum_n a_{nk} c_n^\dagger \quad (\text{so, by orthogonality, } c_n^\dagger = \sum_k a_{nk} c_k^\dagger)$$

where it has been assumed that the matrix a is real, and the spin suffix has been suppressed (as it will be throughout this chapter, except where necessary). Then the total energy of the system will be given by:

$$E = - \sum_n \sum_k^{\text{occ}} \sum_s^{\text{occ}} (t_0 - \alpha(u_{n+1} - u_n)) \cdot 2a_{n+1,k} a_{nk} \\ + \frac{1}{2} K \sum_n (u_{n+1} - u_n + C)^2 + S \sum_n (-1)^n u_n$$

Stafstrom and Chao minimised the energy with respect to the effective bond lengths $(u_{n+1} - u_n)$, but inclusion of the last term above prohibits us from doing this, and the condition that we have an energy minimum gives:

$$0 = - \sum_n (t_0 - \alpha(u_{n+1} - u_n)) \frac{\partial}{\partial u_m} \left(\sum_k^{\text{occ}} \sum_s^{\text{occ}} 2a_{n+1,k} a_{nk} \right) \\ + \sum_n \alpha \frac{\partial}{\partial u_m} (u_{n+1} - u_n) \cdot \left(\sum_k^{\text{occ}} \sum_s^{\text{occ}} 2a_{n+1,k} a_{nk} \right) \\ + K \sum_n (u_{n+1} - u_n + C) \frac{\partial}{\partial u_m} (u_{n+1} - u_n + C) \\ + S \sum_n (-1)^n \frac{\partial}{\partial u_m} (u_n)$$

The first term is difficult to evaluate, but will vanish at self-consistency and is omitted. The remainder of the equation can then be condensed into:

$$0 = 2\alpha \sum_k^{\text{occ}} (a_{mk} a_{m-1,k} - a_{m+1,k} a_{mk}) + K (2u_m - u_{m-1} - u_{m+1}) + S (-1)^m \quad (2.2)$$

assuming that we are in the interior of the chain. When considering the atoms at the ends of the chain, we can use either periodic or simple boundary conditions with only slight alterations. Expressing (2.2) in matrix form, we have:

$$M \cdot u = F$$

with $M_{ij} = -2\delta_{ij} + \delta_{i,j+1} + \delta_{i,j-1}$

$$\text{and } F_m = (2\alpha/K) \sum_k \sum_s^{\text{occ occ}} (a_{mk} a_{m-1,k} - a_{m+1,k} a_{mk}) + (-1)^m (S/K)$$

Again, the above expressions assume that we are in the interior of the chain. If simple boundary conditions apply, the matrix M is tri-diagonal; with PBC's, there are terms at the off-diagonal corners ($M_{1N}=M_{N1}=1$), but M can always be made tri-diagonal by ignoring its last row and column (in general, the standard numerical routines for matrix solution work substantially more quickly for tri-diagonal matrices than for general matrices, which is the reason for seeking to put M into this form).

The justification for the reduction of M to tri-diagonal form in this manner is that M is singular and does not lead to a unique solution for u (consider adding a constant to each element of u , which represents an overall translation in space and cannot lead to an energy change). We can therefore arbitrarily set $u_N=0$, which is equivalent to removing the last column of M , leaving us with N consistent equations in $N-1$ unknowns. The last equation (represented by the last row of M) is clearly redundant and can be dropped too.

It should be noted here that plotting $\tilde{u}_n$ against n will not give a smooth curve in all cases, since the equilibrium bond length is changed slightly (by something like $6 \times 10^{-4}L$) in the presence of a defect; this, because of the factor $(-1)^n$, will lead to rapid apparent oscillations in u . This problem is circumvented by using instead the dimerisation parameter d_n of §1.3, representing the difference between neighbouring bond lengths, which is found to vary smoothly along a chain (this is one reason for choosing a dimerisation parameter defined in this way).

The self-consistency program runs on the IBM 3084 mainframe at Harwell, and currently has an upper limit of 140 carbon units, although the machine constraints would allow for a very much larger upper limit. This limit was chosen in order to be comparable to the "real" length of a typical t-PA

chain, and is very much larger than a typical defect (which extends over something like 10-20 carbon units). It is necessary to choose an initial geometry from which to start the relaxation process; the particular geometry chosen should not affect the results, since these are self-consistent, but will determine the time that the program takes to reach a converged solution. The initial geometries used were, therefore, usually chosen to be reasonable approximations to the actual geometries of the defects. In order to rule out the possibility that they had affected the self-consistent results in some way, for example by imposing some sort of symmetry constraint, a number of the calculations were repeated with the initial geometry of an undimerised or uniformly dimerised chain. In all cases, this had no effect on the final results.

It was assumed, when considering charged chains, that the occupied electronic eigenstates were always those of lowest energy; thus a chain of length 100, with a single positive charge imposed, was treated by filling the lowest 50 eigenstates of one spin and the lowest 49 of the other spin. Since the equations dictating how the atomic co-ordinates depend on the electronic wave functions (equation (2.2)) involve a sum over occupied states, it is through the change in the limits of this summation that the charge on a chain affects the chain geometry.

2.3 DEFECT GEOMETRY AND BAND STRUCTURE OF t-PA

There are no great surprises to be had on plotting the band structure of t-PA. In fig. 2.1, the eigenvalues of the undimerised chain are shown, and are given by $E_k = -2t_0 \cos ka$, as predicted by Hückel theory. Dimerisation opens up a band gap, as shown in fig. 2.2, and the new eigenvalues are given by $E_k^2 = (2t_0 \cos ka)^2 + (4\alpha_0 \sin ka)^2$, corresponding to a band gap of $8\alpha_0$. In fig. 2.3, the eigenvalues of a chain with two (well separated) solitons are plotted, showing how the new states have energies at midgap (i.e. zero, since we have defined this to be the energy of a localised p_z

orbital). Then in fig. 2.4, the eigenvalues resulting from the removal of an electron are plotted. These are equivalent to those generated by adding an electron, by charge conjugation symmetry, of which more will be said in §3.6. As stated in §1.5, the resulting polaron leads to eigenvalues spaced symmetrically about midgap, at $\pm 0.48\text{eV}$.

The geometry of a chain of t-PA, of length 100 and with periodic boundary conditions, is plotted in figs. 2.5-2.10, as the number of electrons removed is increased. Fig. 2.5 shows how the geometry of a polaron consists of a fairly light distortion in the local dimerisation. fig. 2.6 indicates how this has decayed into two solitons on removal of a second electron, again as predicted in chapter 1. Removal of a third charge (fig. 2.7) leads to the formation of a polaron in addition to this soliton pair; the soliton states are both empty, so the only place from which we can remove this third electron is the valence band. This is entirely analogous to the process that formed the first polaron, so the presence of the soliton pair on the chain has no effect on its behaviour on being charged again. At this stage (3% doping) the defects are free to exist independently, but addition of a fourth charge (fig. 2.8) leads to what looks like the start of defect interaction, by the formation of a "soliton lattice". By the time six and ten charges have been added (figs. 2.9 and 2.10 respectively) the lattice is clear; note that the maximum dimerisation has been significantly reduced from its ground state value by this time.

The way that the defect-induced distortion manifests itself in the band structure is shown in figs. 2.11-2.13, which show how the band structure changes when 4, 6 and 10 holes are added. In fig. 2.11, the addition of 4 holes is insufficient to lead to appreciable broadening of the soliton "band" at midgap (recall that the width of a soliton is only ≈ 14 carbon units), but by the time that 6 or 10 holes have been added the broadening is quite significant and the band structure rather resembles that of undimerised (metallic) t-PA. This is in line with the estimate of Ikehata

et al. (1980) that t-PA undergoes a semiconductor-metal transition at around 7-11% doping.

2.4 SELF-CONSISTENT CALCULATIONS ON NON-DEGENERATE POLYMERS

Application of the modified SSH Hamiltonian to polymers without a degenerate ground state leads to results plotted in figs. 2.14-2.17. Figs. 2.14 and 2.15 show how the distortion around a polaron is reduced as the degeneracy-breaking parameter S is increased, which seems intuitively reasonable; figs. 2.16 and 2.17 show the same result for bipolarons (which are now, of course, stable with respect to two-soliton decay, due to the non-degeneracy; stability with respect to two-polaron decay is no longer automatic in principle, but always bound to occur in the SSH model due to its lack of any term representing the electron-electron interaction). Note how the degree of ground state dimerisation is increased by increasing S ; consideration of the extra energy term represented by this non-degeneracy accounts for this (note also how the minimum of fig. 1.6 is shifted to higher u_0 by addition of the extra term).

How the energies of the polaronic (and bipolaronic) eigenstates are affected by this extra term is summarised below (Δ is used to represent half the band gap; remember that the states occur in pairs symmetrically spaced about the band gap):

	<u>S=0</u>		<u>S=0.4</u>		<u>S=1.0</u>	
Band gap	1.40eV		1.65eV		1.93eV	
Polaron states	0.48eV	0.66 Δ	0.61eV	0.74 Δ	0.77eV	0.79 Δ
Bipolaron states	(0.0)		0.28eV	0.34 Δ	0.45eV	0.46 Δ

It is clearly reasonable that the defect states move towards the band edges as the degree of non-degeneracy increases and the defect-induced distortion decreases; Fesser *et al.* (FBC) (1983), using the continuum model of Takayama *et al.* (TLM) (1980) predicted similar results, with polaron states at $\pm\Delta/2$ for t-PA; in view of the approximations involved in deriving the

TLM model, this appears to be excellent agreement.

2.5 PREDICTIONS FOR OPTICAL ABSORPTION

We can use the wave functions generated by this self-consistency program to check how the results of Fesser *et al.*, who predicted defect absorption profiles in conjugated polymers, are affected by the use of a discrete numerical system, rather than the TLM continuum model. We calculate the absorption cross-section for Franck-Condon (vertical) transitions from the standard formula (Stoneham 1975, p.272):

$$\sigma(i,f;E) \propto E | \langle f | x | i \rangle |^2 \delta(E_f - E_i - E)$$

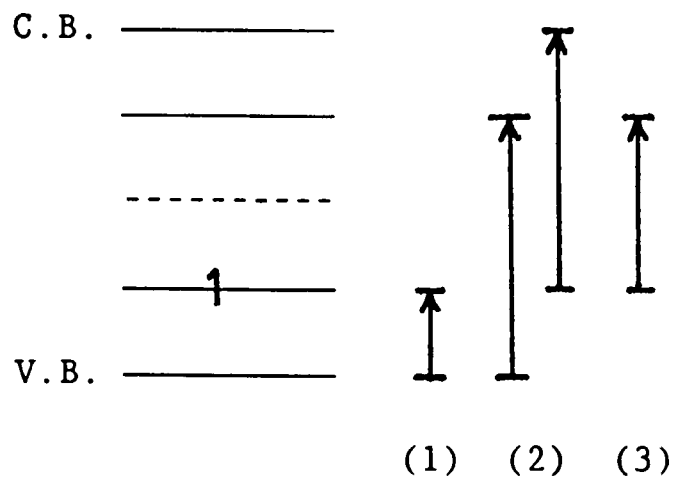
where i and f refer to the initial and final electronic states. In order to make the results more easily comprehensible, they are convoluted with Gaussians of width 0.1eV.

GROUND STATE ABSORPTION. Fig. 2.18 shows the predicted absorption of a ground state chain of t-PA; its finite nature has smoothed out the $(1/\sqrt{E})$ singularity predicted at the band gap for an infinite chain, but the general character of the infinite chain absorption pattern remains.

SOLITON ABSORPTION. A soliton will lead to just one extra peak in the absorption spectrum, representing a transition from the valence band to an unoccupied soliton state, or from an occupied soliton state to the conduction band; this absorption should occur at mid-gap. In fig. 2.19, the absorption due to a hole soliton is plotted, showing substantial absorption at this energy (0.7eV) and corresponding bleaching of the band to band absorption (owing to the sum rule).

POLARON ABSORPTION. Fig. 2.20 duplicates the results of FBC for polaron absorption. Labelling the respective absorption components as follows:

- (1) Valence band to lower localised state
- (2) Valence band to higher localised state
- Lower localised state to conduction band
- (3) Lower to higher localised state



we find only peaks due to components (1) and (3), since the calculated matrix elements for both of the two (degenerate) transitions labelled (2) are extremely small. Similar results are obtained for the absorption of c-PA; the absorption of a bipolaron (fig. 2.21) is dominated by peak (1) (peak (3) now being forbidden, and peak (2) still very small). These results are not in agreement with the experimental evidence that the absorptions due to peaks (1) and (2) are comparable; the reason for this anomaly is that the SSH Hamiltonian (even with electron-electron interaction included in the Hubbard-U formalism) displays a spurious *charge conjugation symmetry* (*electron-hole symmetry*) (Sum *et al.* 1988, A.R.Bishop, private communication), which artificially reduces the strength of transition (2) and which will be discussed further in §3.6.

ABSORPTION FROM MULTIPLY CHARGED CHAINS. FBC did not attempt to calculate wave functions (or, therefore, absorption profiles) for chains with more than one defect; this is not a feasible calculation within TLM. Within this numerical model, however, such calculations are routine. Absorption profiles for t-PA chains with 3, 4, 5, 6 and 10 defects are shown in figs. 2.22-2.26. When considering a chain containing both solitons and polarons (e.g. the chain with three holes added, whose dimerisation pattern was shown in fig. 2.7 and whose absorption pattern is shown in fig. 2.22), there is an additional low energy peak, due to the transition between the lower polaron state and the soliton state. For high doping levels, the defect-induced absorption within the gap is substantially stronger than the interband absorption, and the broadening of this absorption due to overlap

of the defects is noticeable.

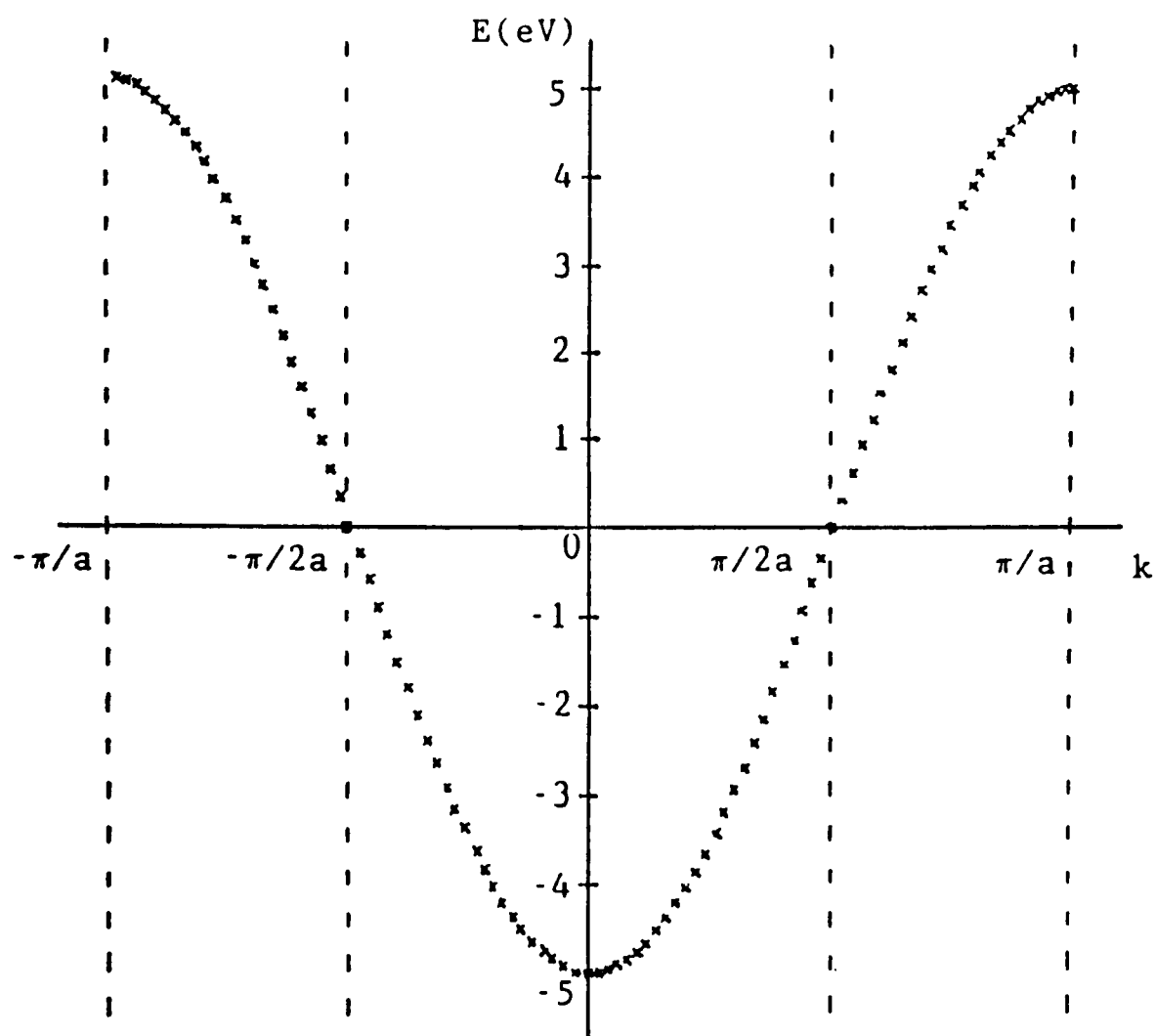


Fig. 2.1 One-electron eigenvalues of undimerised t-PA

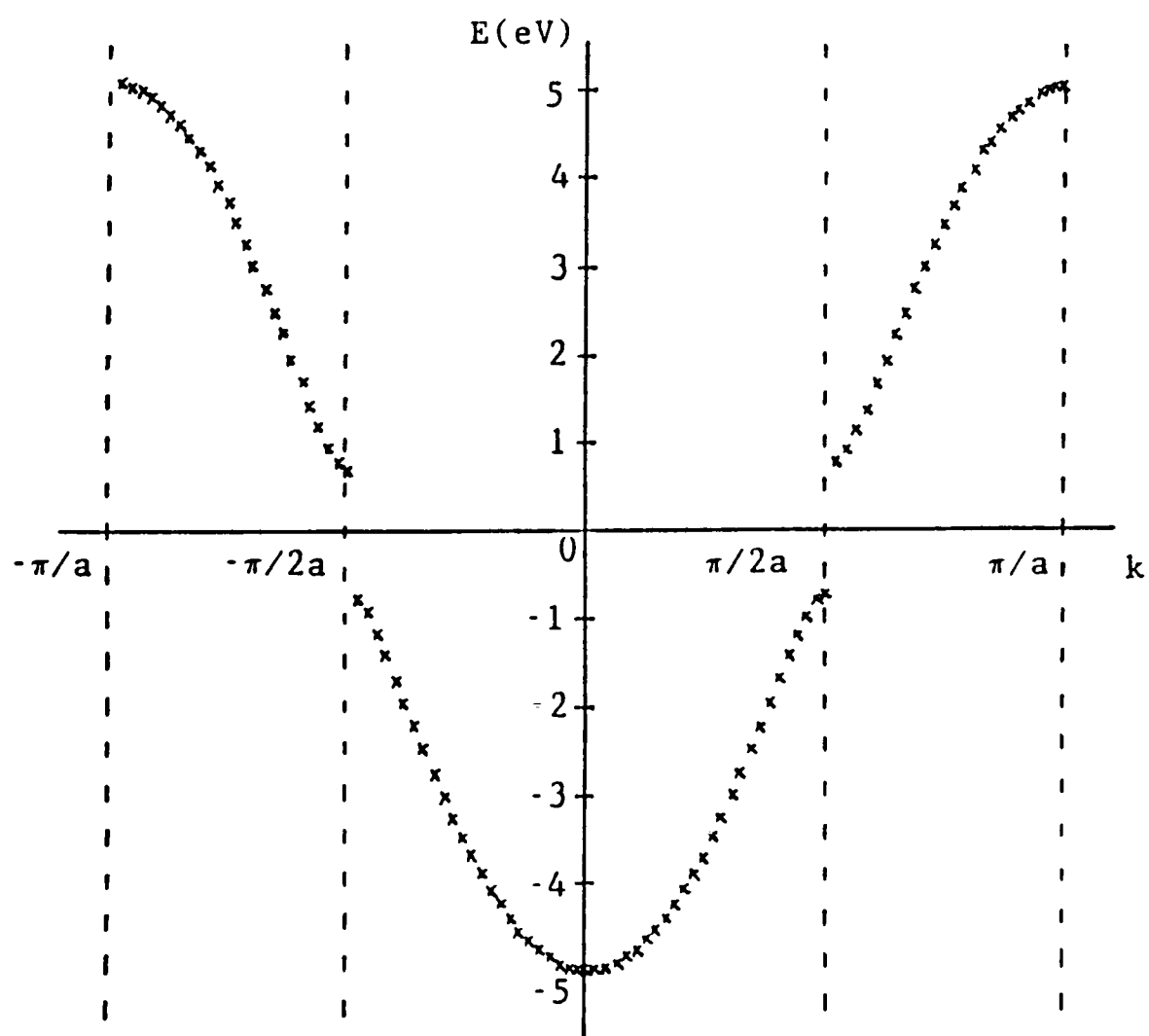


Fig. 2.2 Eigenvalues of dimerised t-PA. Dimerisation has opened up a band gap of approximately 1.4 eV.

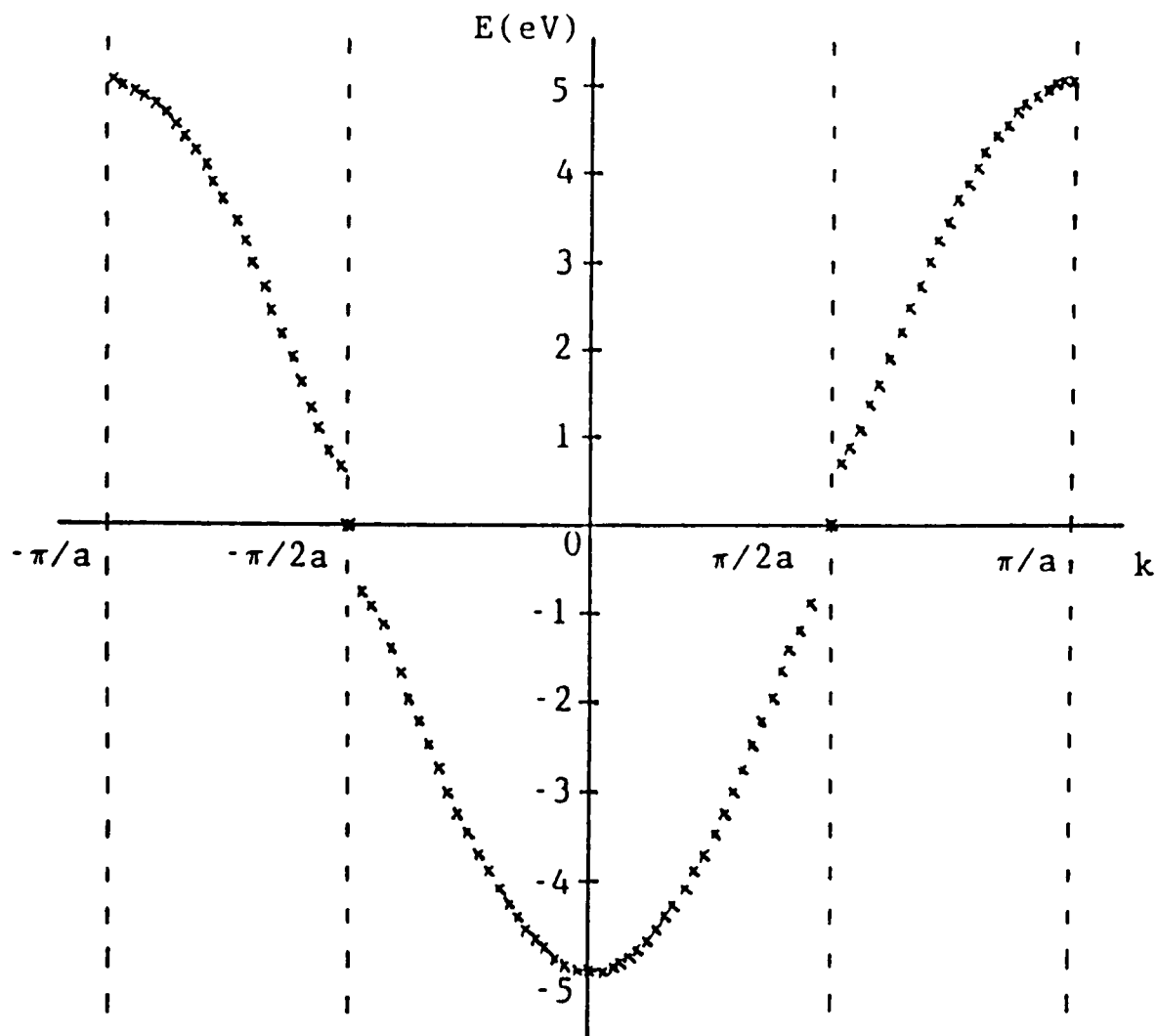


Fig. 2.3 Eigenvalues of a t-PA chain with two isolated solitons. The solitons have energy at midgap, i.e. at $E=0$ on this scale.

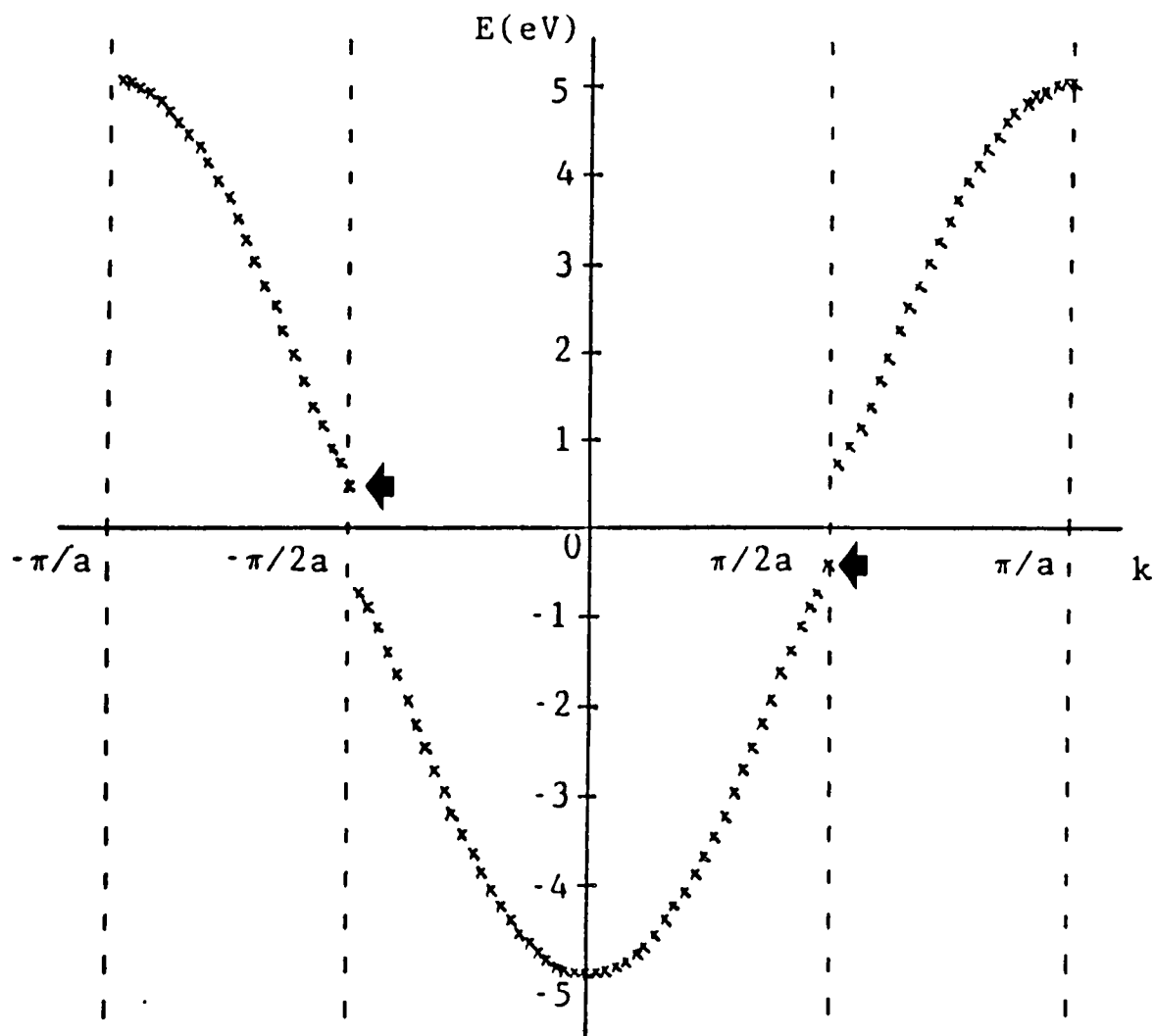


Fig. 2.4 Eigenvalues of a t-PA chain with a polaron. The two localised states associated with the polaron (arrowed) have energies ± 0.48 eV, well within the band gap.

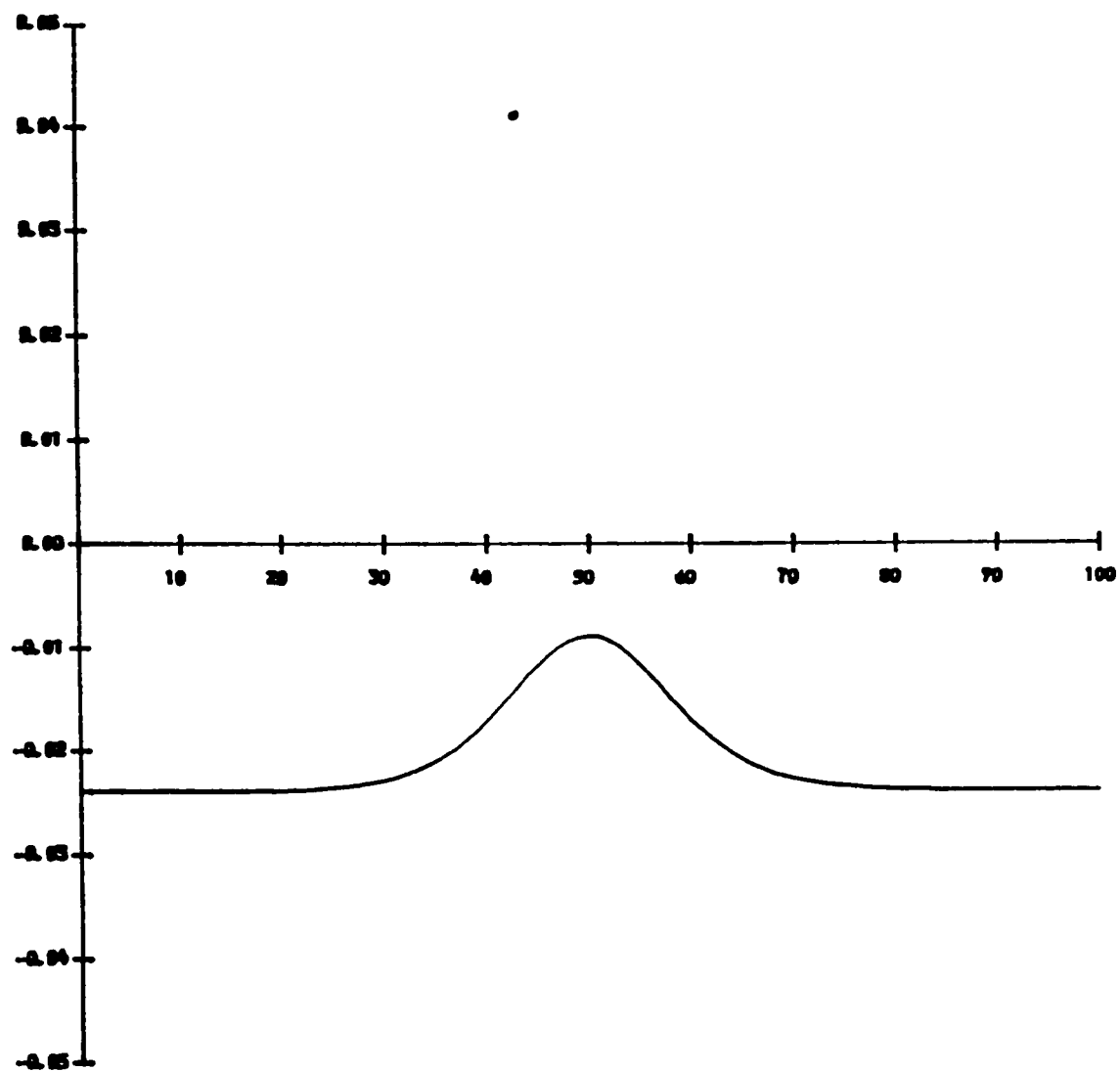


Fig. 2.5 Geometry of a polaron in t-PA. The units used here, as in figs. 2.6-2.10, are such that the ground state dimerisation of t-PA is 0.024. Periodic boundary conditions are used for all of these figures.

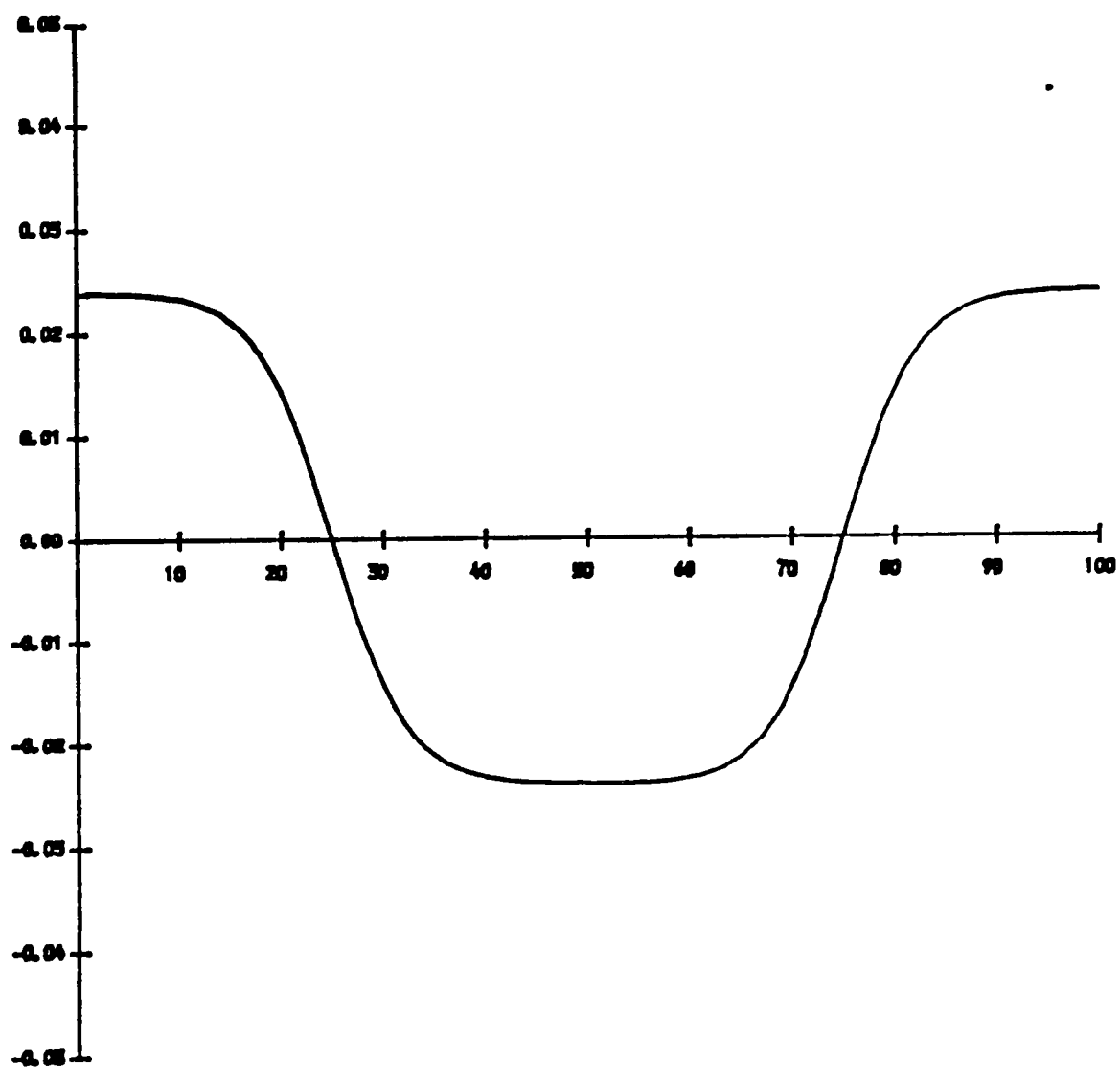


Fig. 2.6 Isolated soliton pair in t-PA

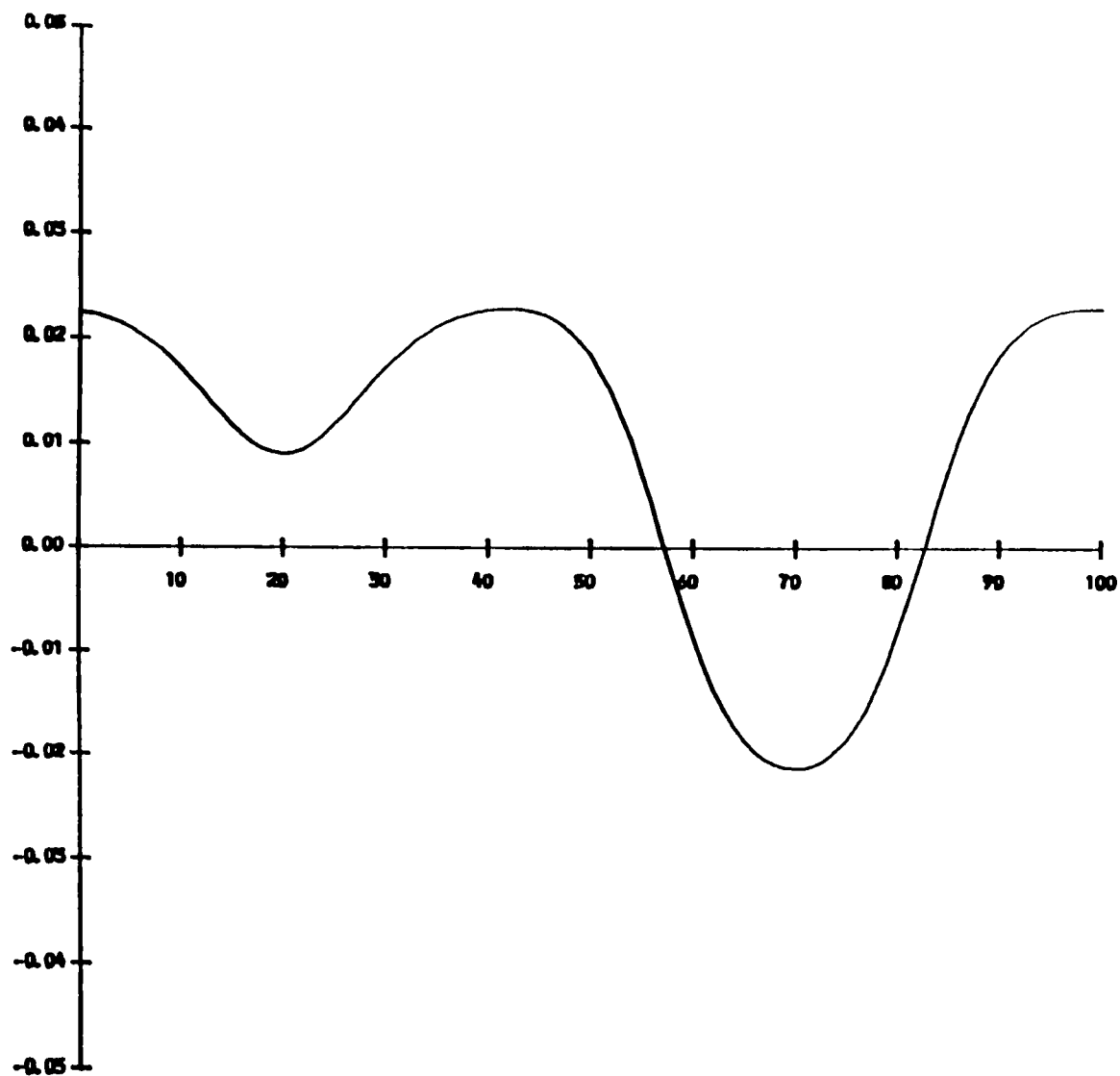


Fig. 2.7 Distortion resulting from the removal of three electrons from a t-PA chain. Note that the three defects formed (two solitons and a polaron) are still virtually isolated.

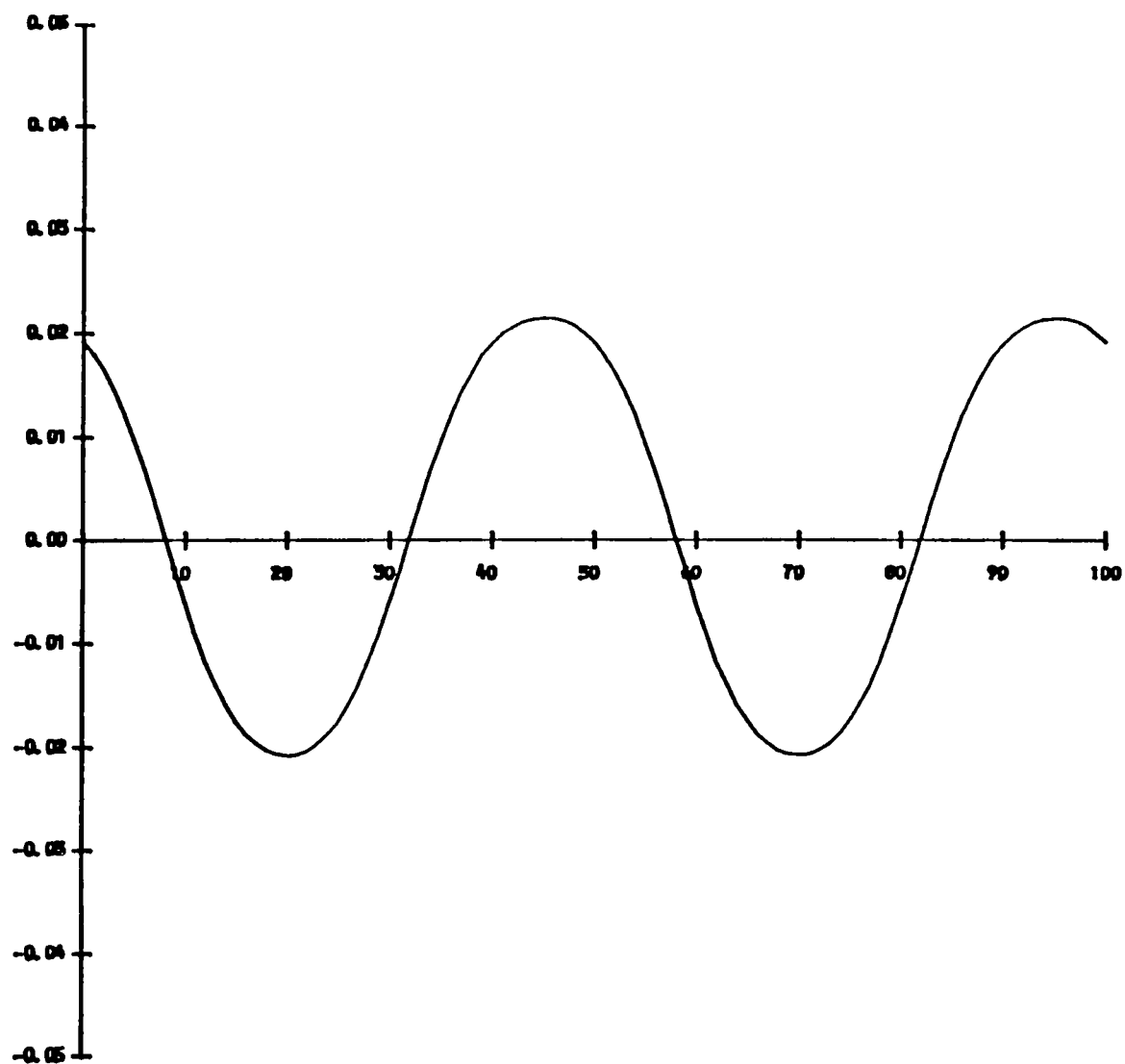


Fig. 2.8 Distortion resulting from the removal of four electrons from a t-PA chain. Although the solitons are evenly spaced along the chain, the interaction between them is still small, as is evidenced by the fact that the maximum value of the dimerisation is still close to the ground state value.

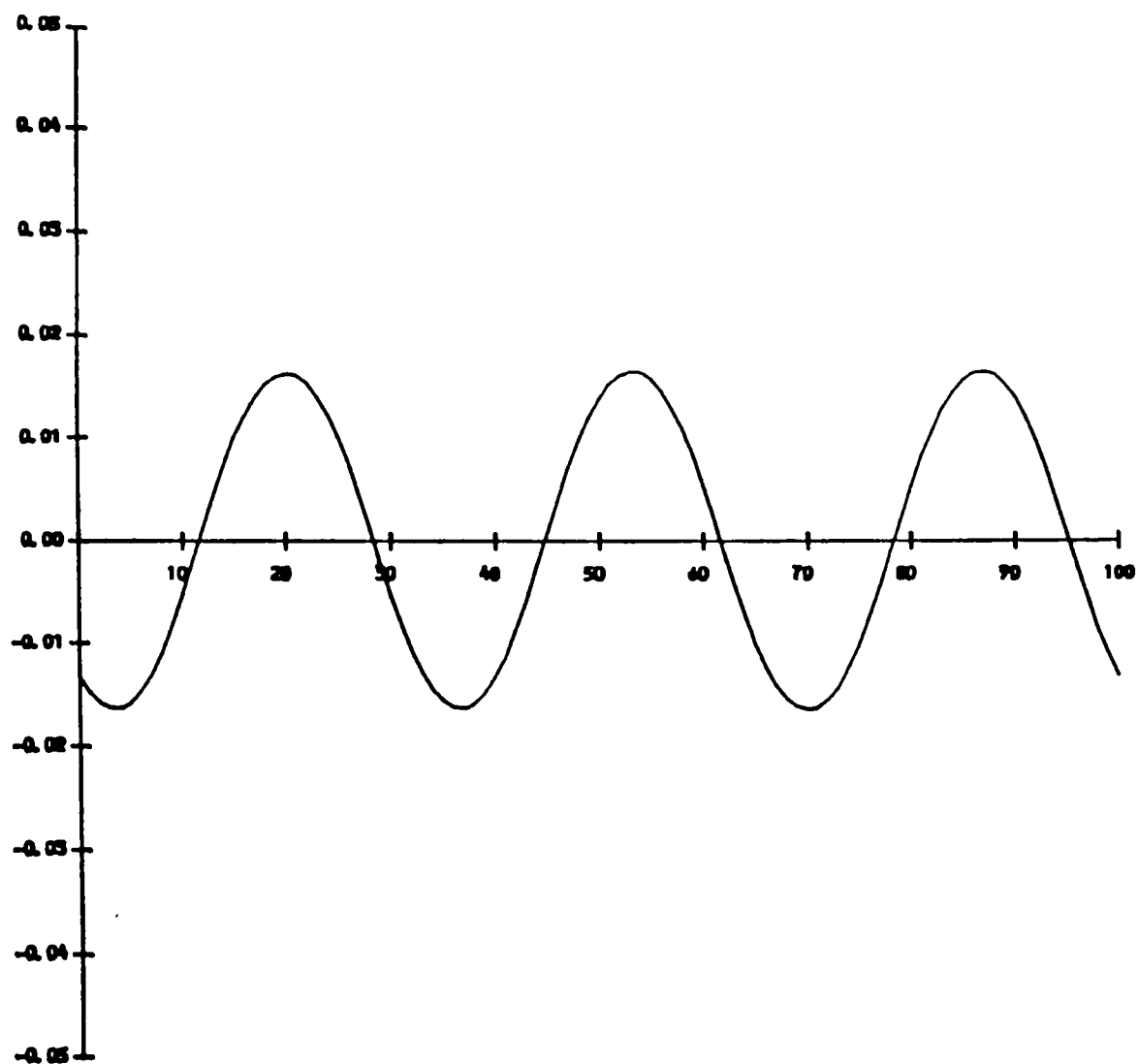


Fig. 2.9 Distortion resulting from the removal of six electrons from a t-PA chain. The solitons are now interacting sufficiently to reduce the maximum extent of dimerisation by a significant amount from its ground state value, and the formation of a soliton lattice is clear.

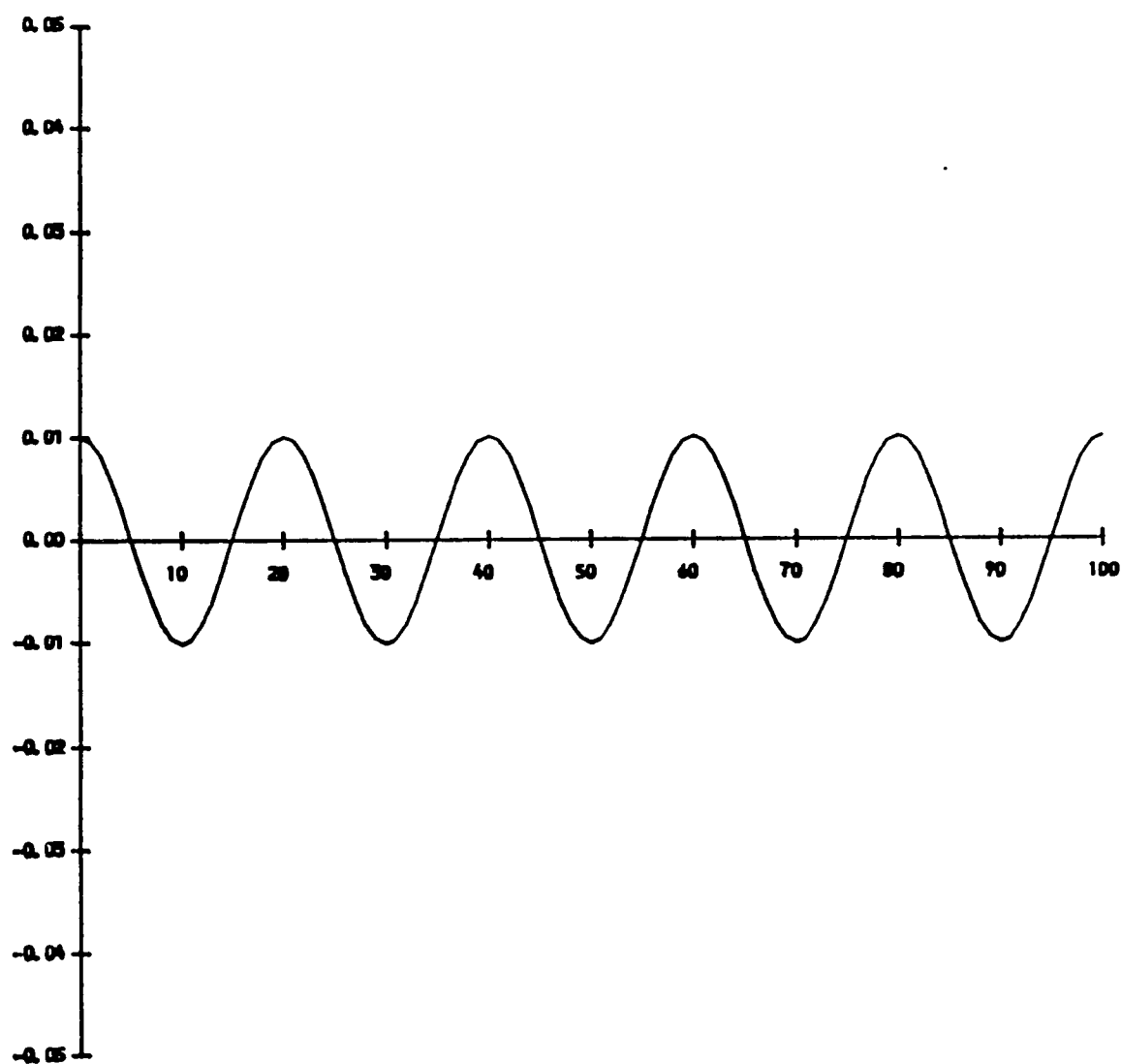


Fig. 2.10 Distortion resulting from the removal of ten electrons from a t-PA chain. The maximum dimerisation is now only 40% of its ground state value.

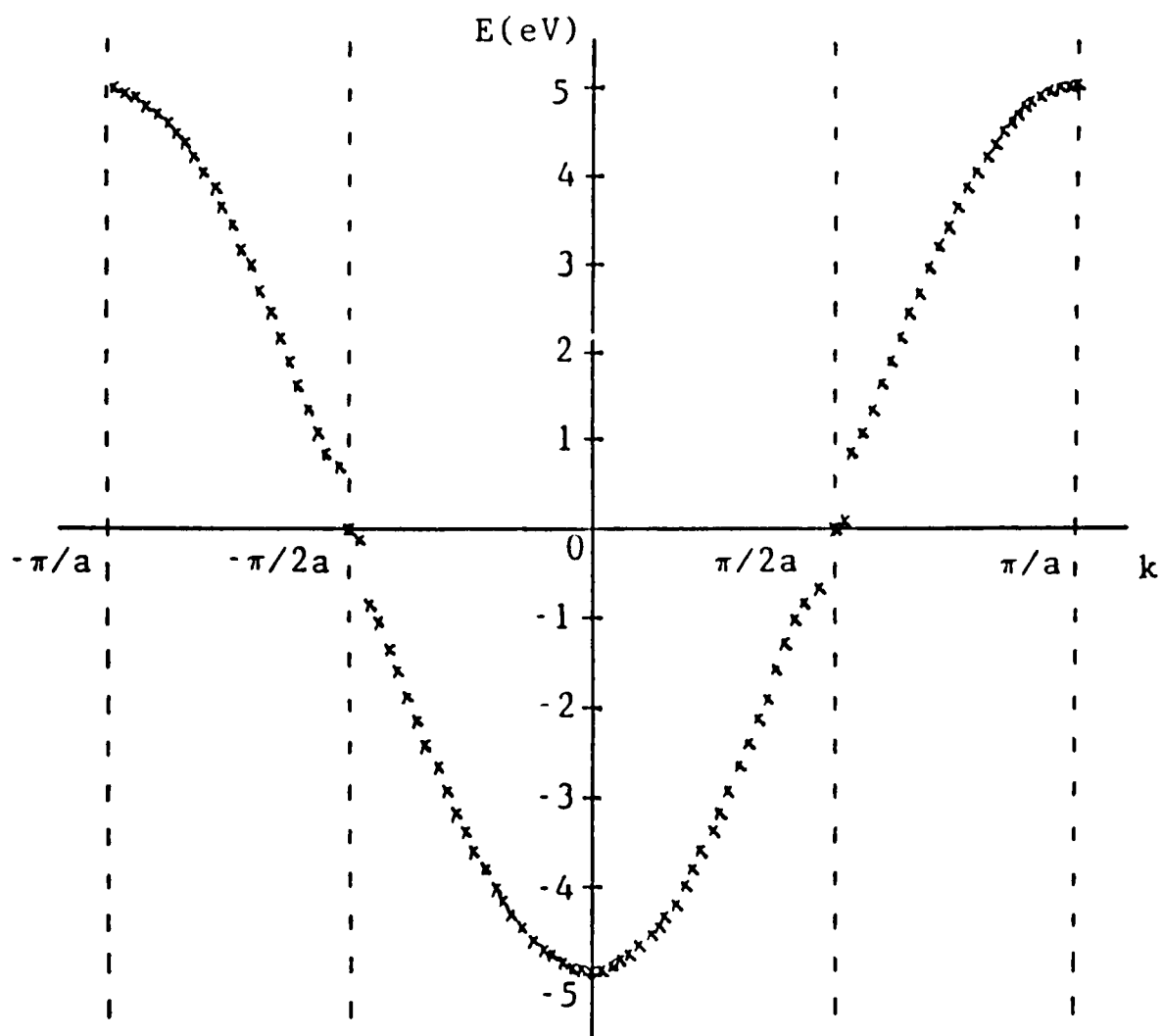


Fig. 2.11 Eigenvalues of a t-PA chain with four holes (whose geometry was plotted in fig. 2.8). Note that the overlap between the solitons is insufficient to move their energies away from midgap by any great amount.

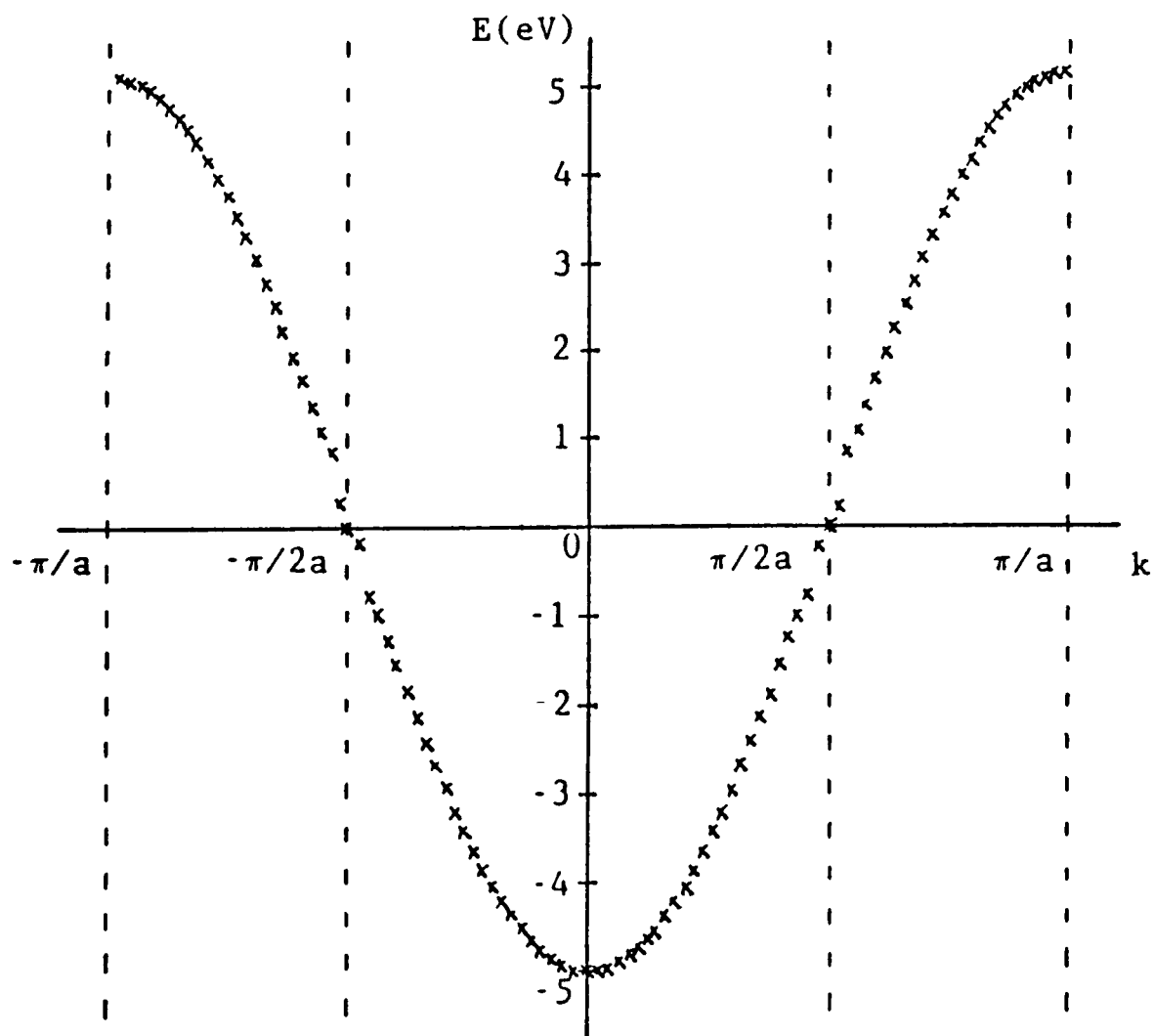


Fig. 2.12 Eigenvalues of a t-PA chain with six holes (cf. fig. 2.9). It is now clear that the solitons are overlapping and forming a band.

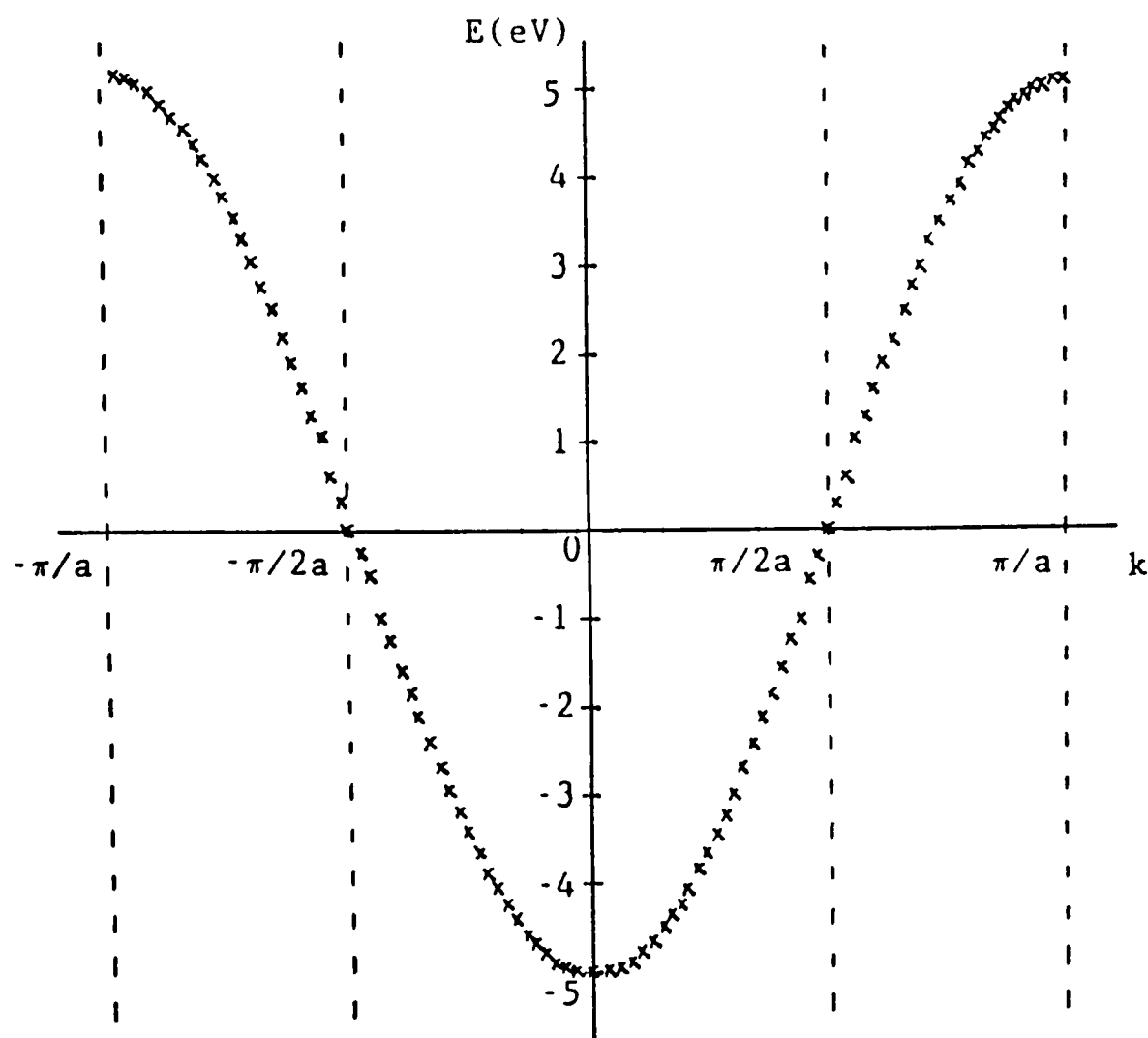


Fig. 2.13 Eigenvalues of a t-PA chain with ten holes (cf. fig. 2.10). The soliton band is now sufficiently broad that the dispersion relation resembles that of the undimerised, metallic form (fig. 2.1). This is in agreement with experimental estimates that t-PA undergoes a semiconductor-metal transition at about 7-11% doping (see§2.3).

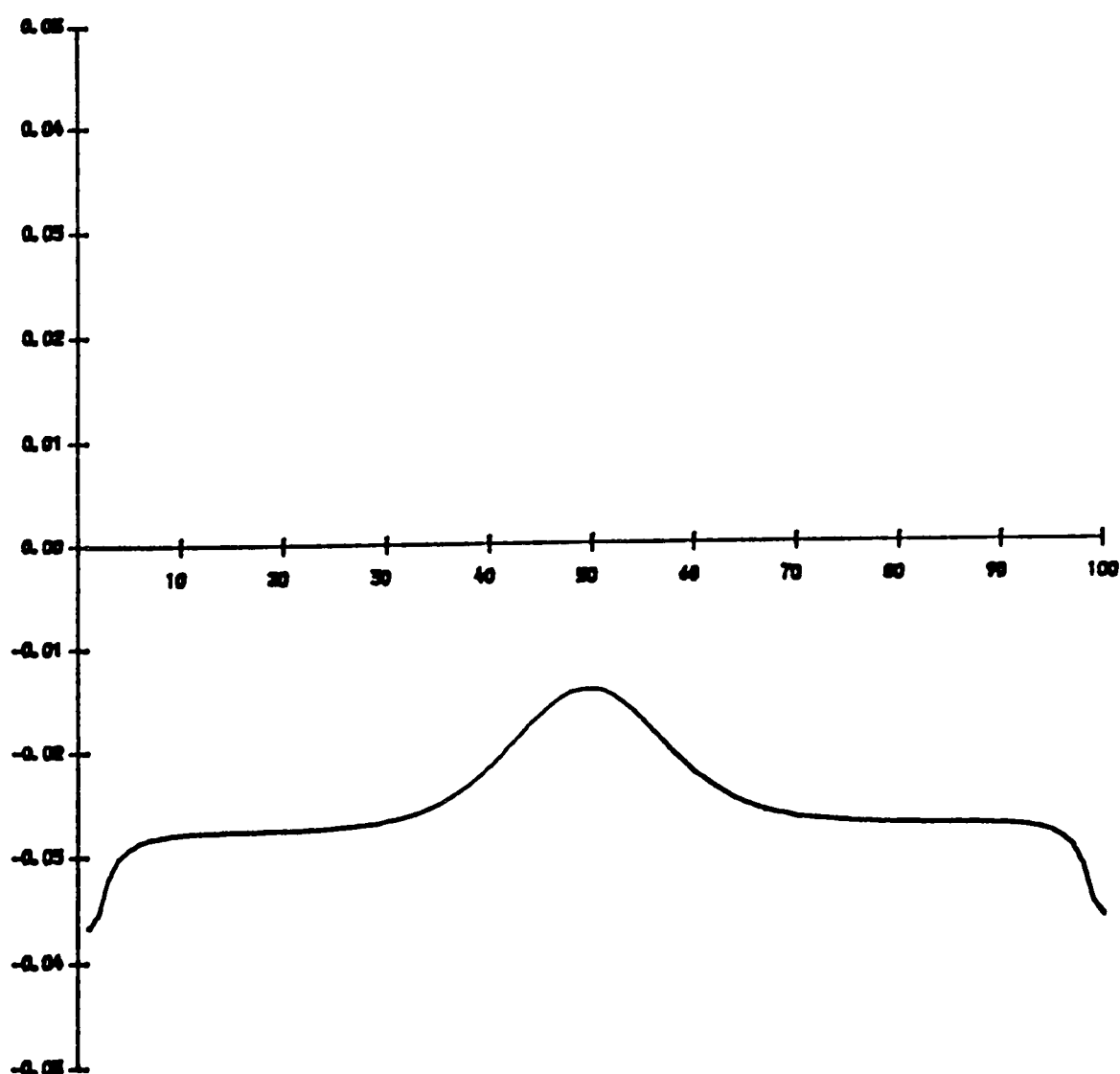


Fig. 2.14 Polaron in a non-degenerate polymer, with $S=0.4$ (see (2.1)). The distortion is slightly shallower and more localised than its equivalent in t-PA (fig. 2.5); note how the dimerisation is enhanced at the ends of the chain (periodic boundary conditions were not used for these calculations).

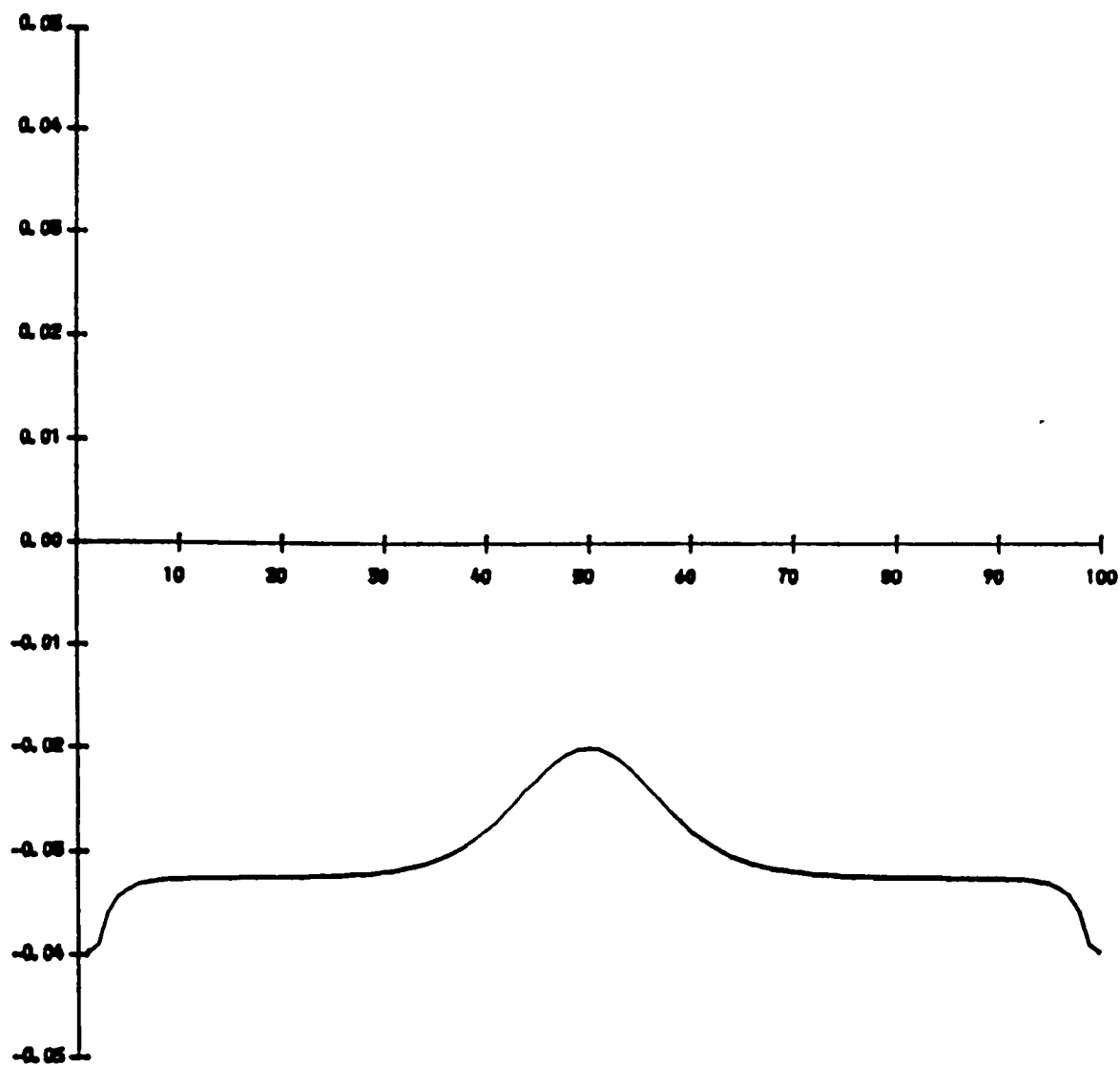


Fig. 2.15 As fig. 2.14, but with $S=1.0$, used as a model for c-PA. The polaron is shallower still, and the ground state dimerisation amplitude is significantly increased from its value in t-PA.

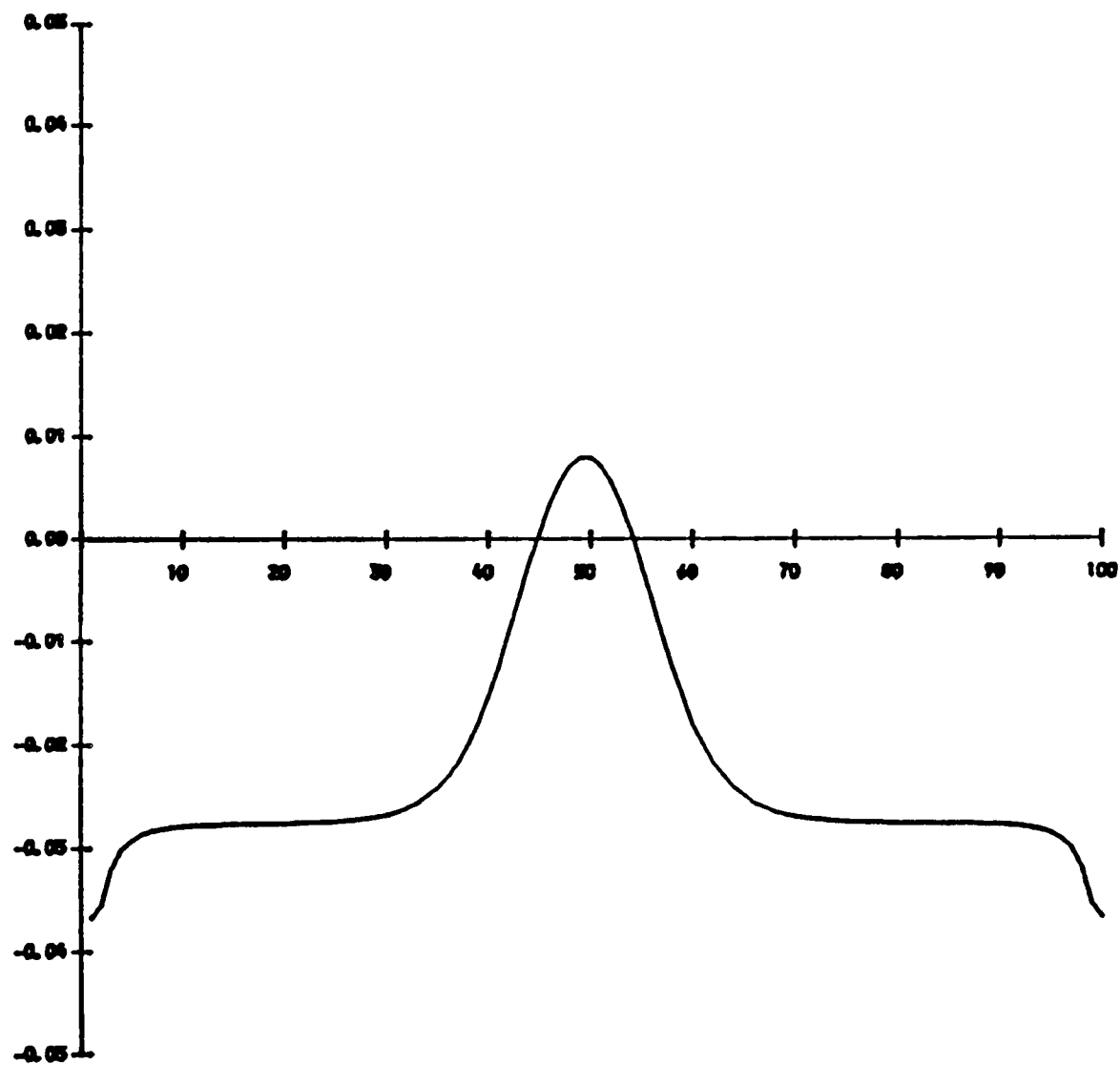


Fig. 2.16 Bipolaron in a non-degenerate polymer, with $S=0.4$. The non-degeneracy means that the two defect states associated with a bipolaron are no longer free to separate into a soliton pair as in fig. 2.6.

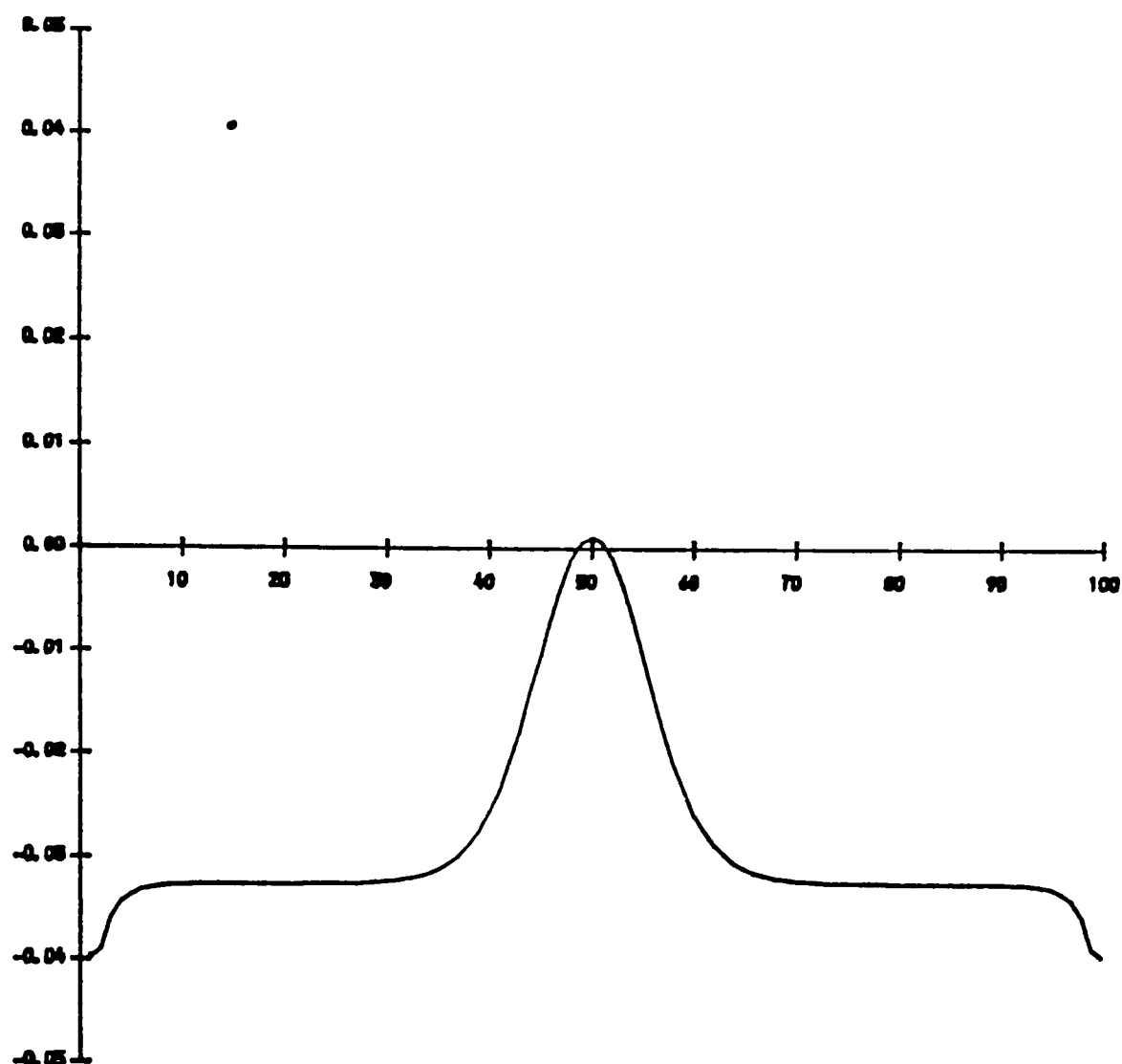


Fig. 2.17 As fig. 2.16, but with $S=1.0$. The calculated depth of the distortion will be important when considering the question of photoluminescence in c-PA in chapter 7. Note that the SSH model predicts an identical shape for the exciton, owing to charge conjugation symmetry (see §3.6 for a discussion of this symmetry).

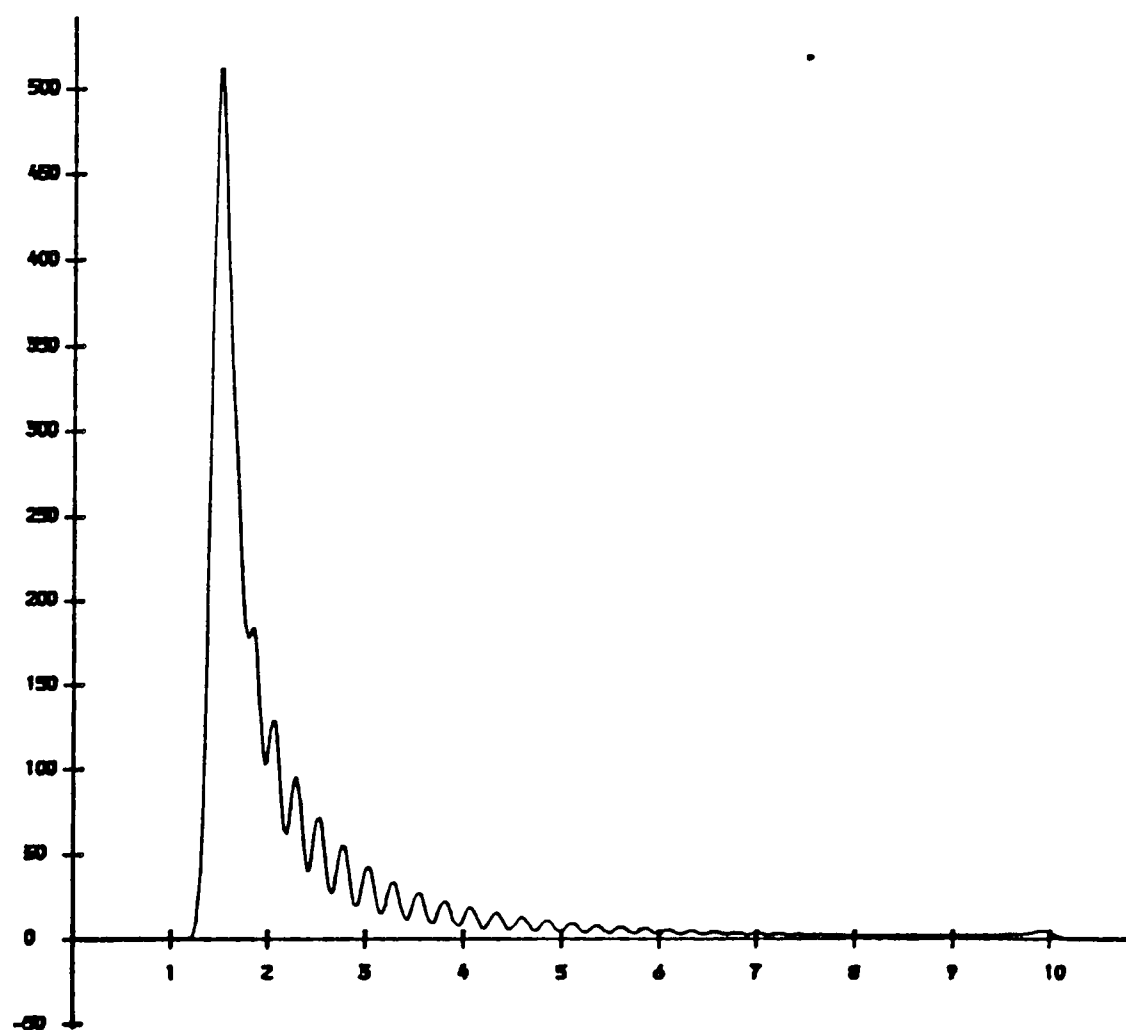


Fig. 2.18 Ground state optical absorption spectrum of t-PA (arbitrary units). In all of the optical absorption spectra presented here, the calculated spectra have been convoluted with Gaussians of half-width 0.1 eV in order to make the results more easily comprehensible.

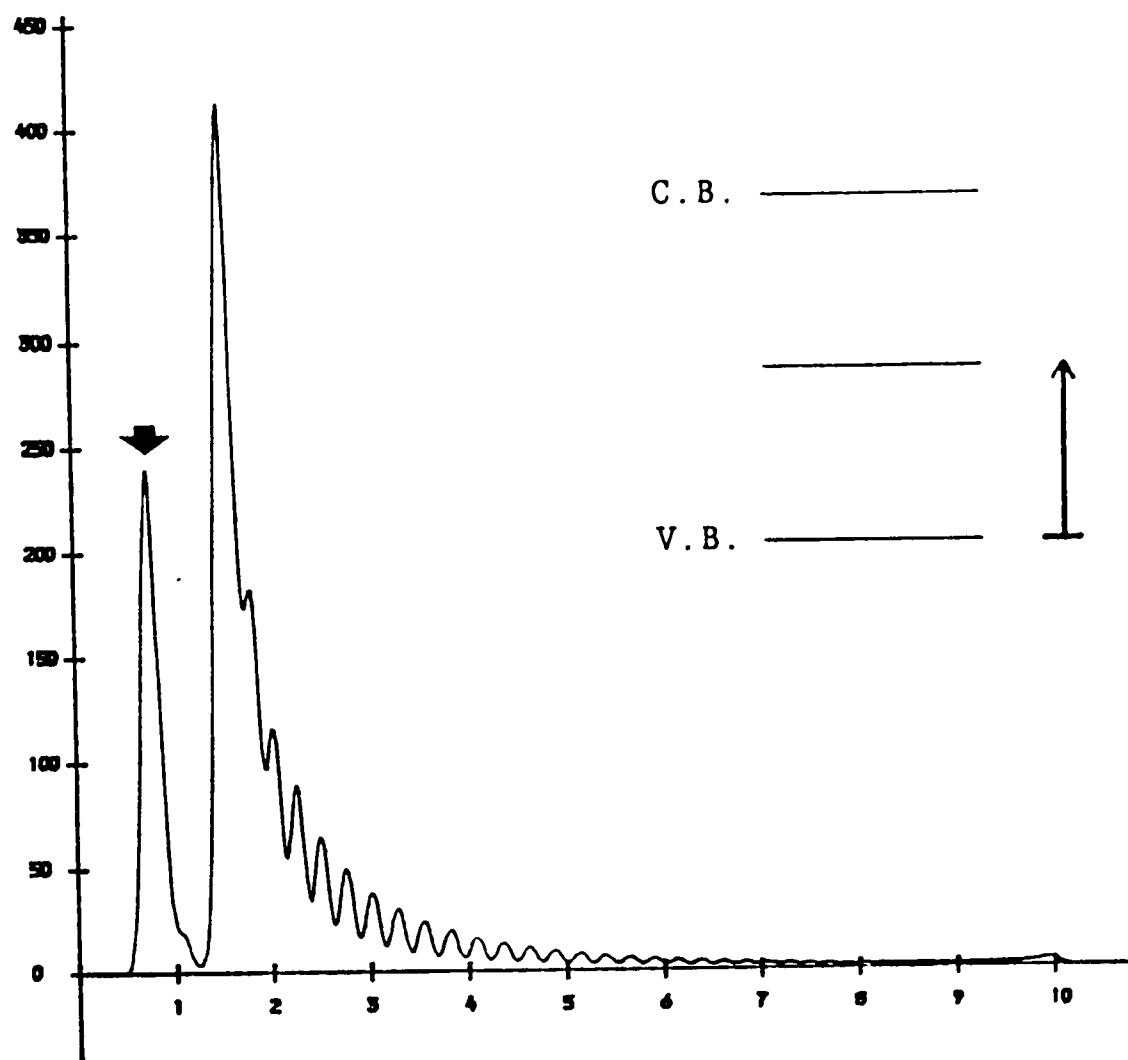


Fig. 2.19 Absorption of t-PA with a soliton. The arrowed peak corresponds to the valence band to soliton transition (see inset); the remainder of the absorption is interband.

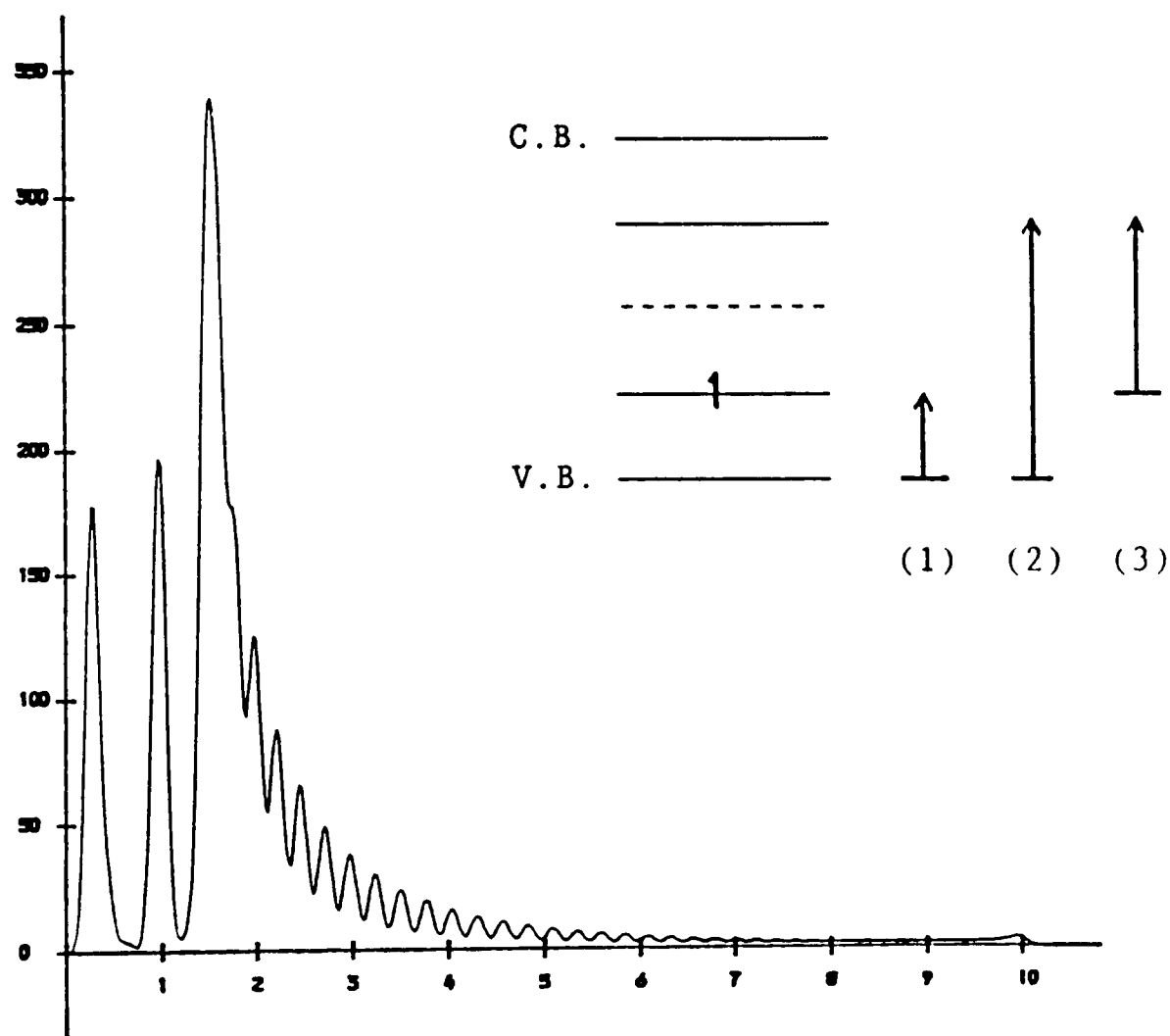


Fig. 2.20 Absorption of t-PA with a polaron. The peaks within the gap correspond to transitions labelled (1) and (3) in the energy level diagram; the matrix element calculated for transition (2) is so small that the corresponding absorption peak is not visible.

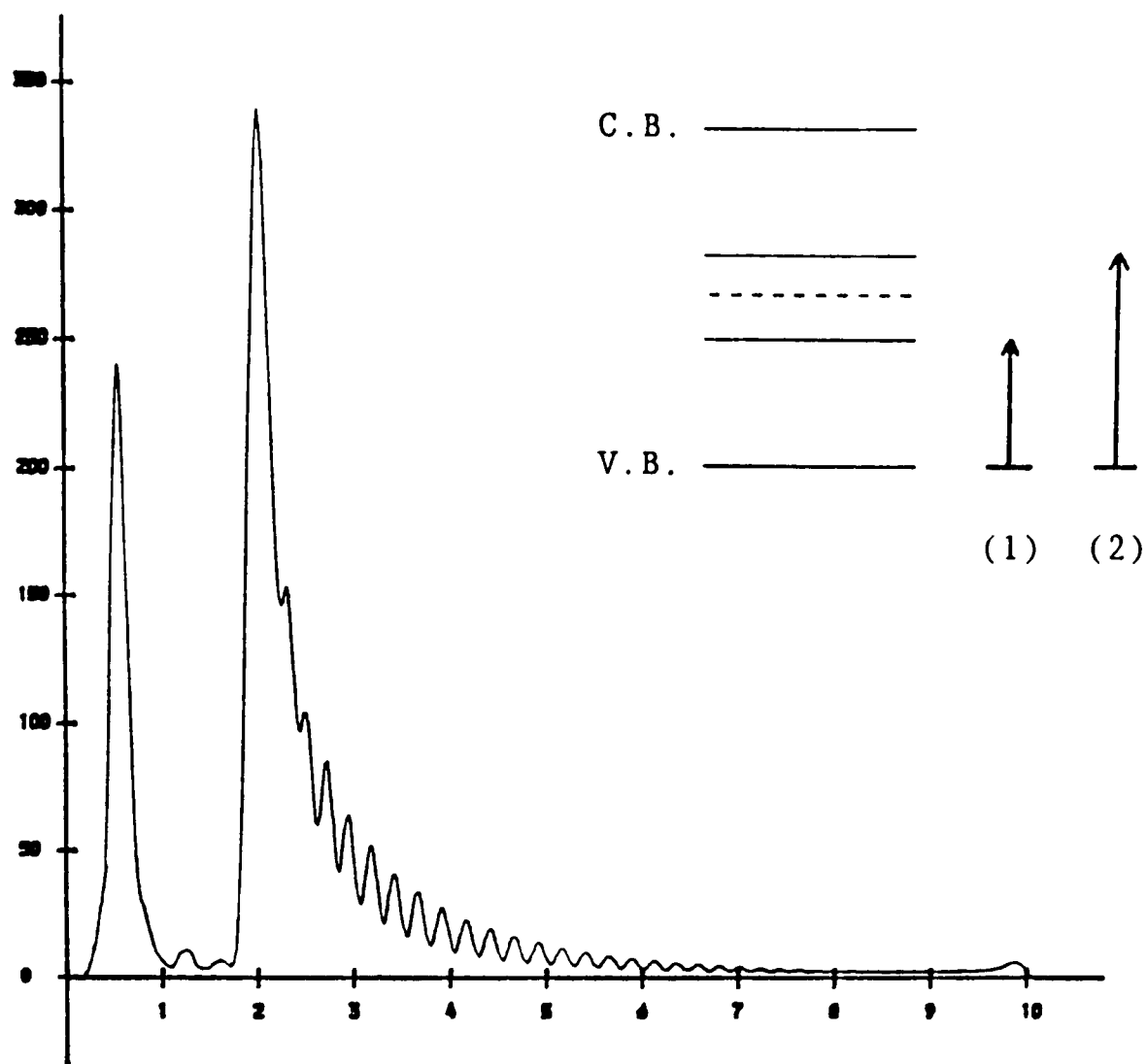


Fig. 2.21 Absorption of c-PA with a bipolaron. Only two transitions are now allowed; again, the matrix element calculated for transition (2) is very small, so transition (1) dominates the interband absorption.

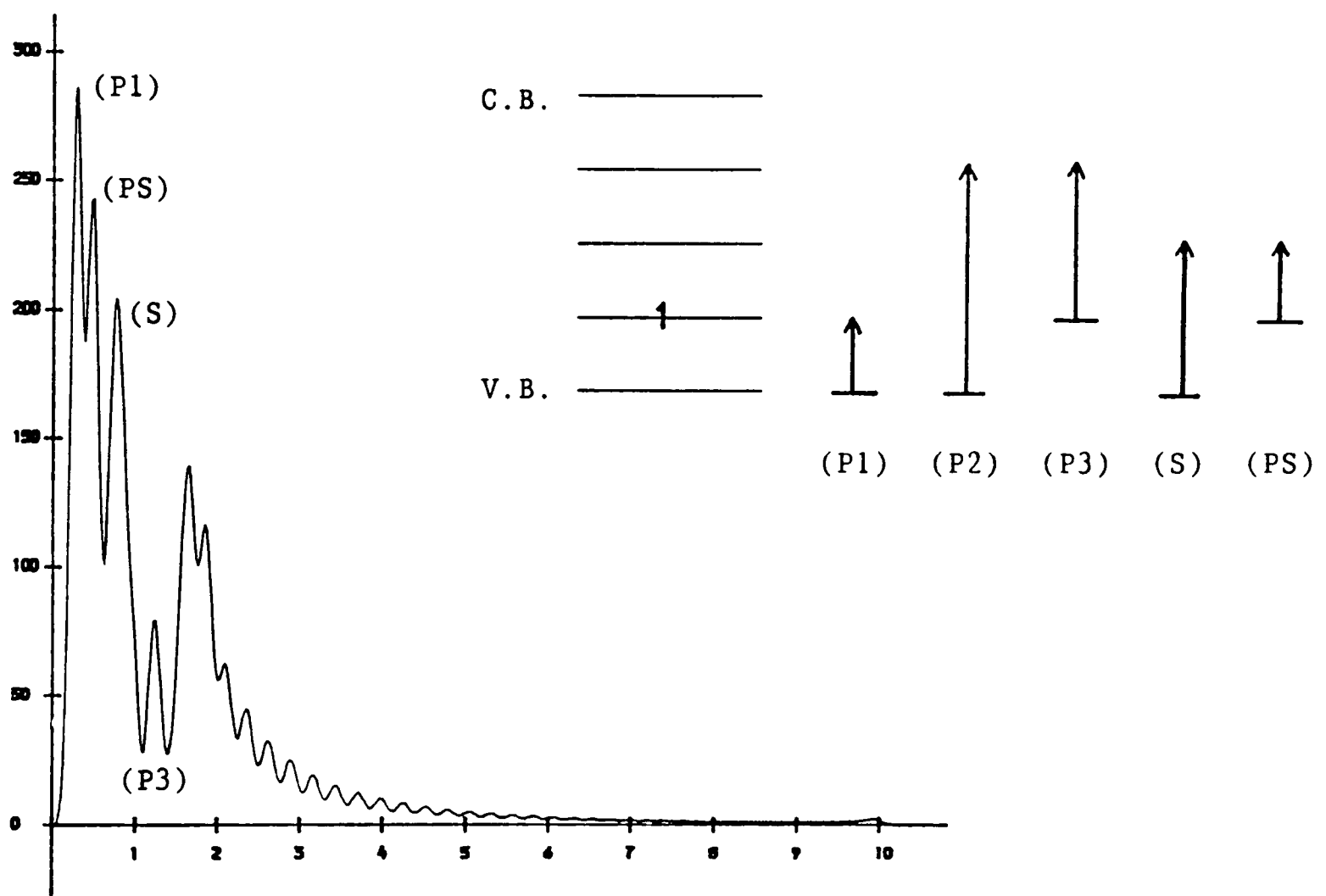


Fig. 2.22 Absorption of t-PA with three electrons removed. There are now four peaks observable within the gap: the two polaron peaks (P1) and (P3), with the third polaron transition (P2) still too weak to be observed, plus the soliton peak labelled (S) and the polaron to soliton transition (PS).

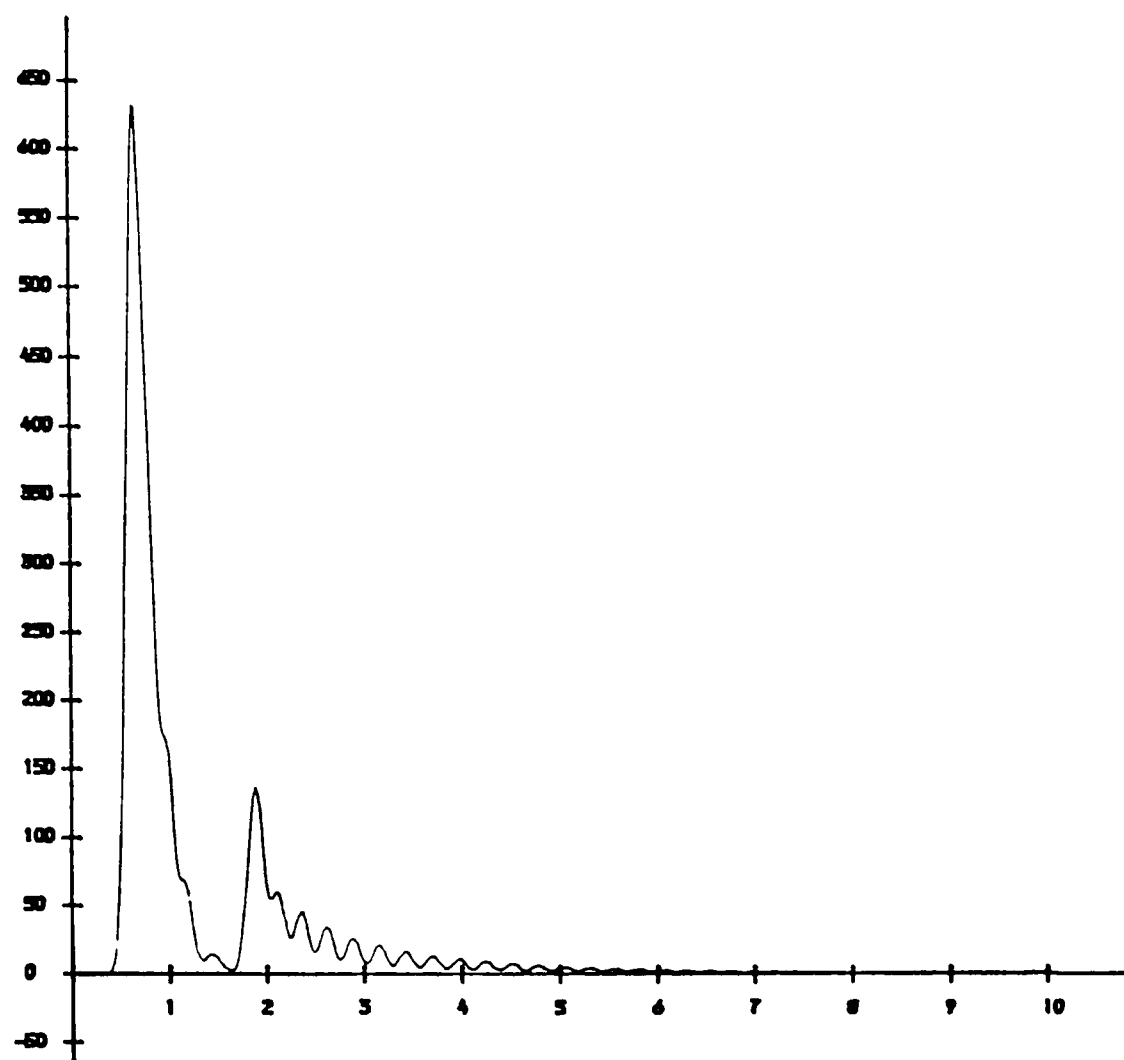


Fig. 2.23 Absorption of t-PA with four electrons removed. There are now four solitons on the chain, and the total valence band to soliton transition is sufficient to swamp the interband absorption.

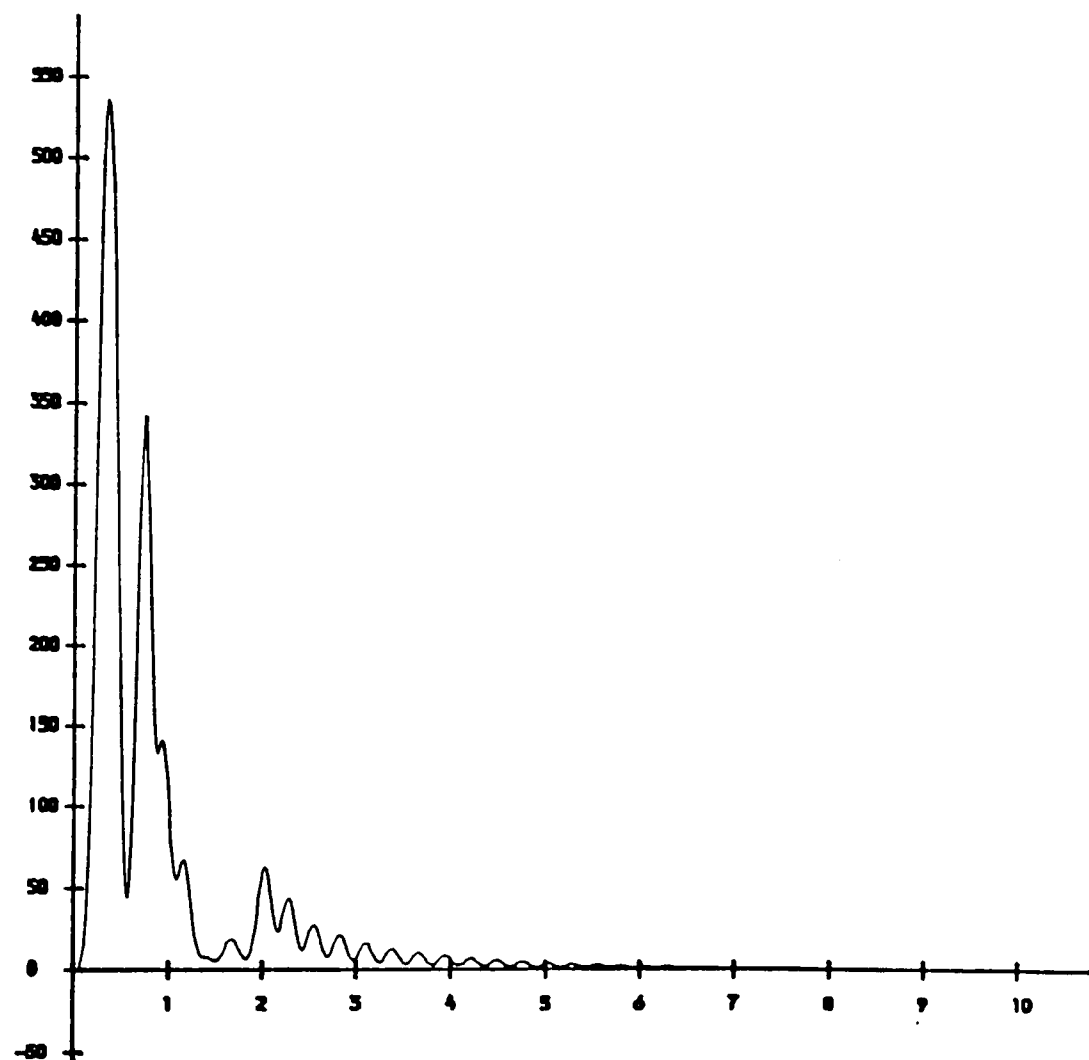


Fig. 2.24 Absorption of t-PA with five electrons removed. Interaction between the solitons has smeared the sharp peaks of fig 2.22 into two bands.

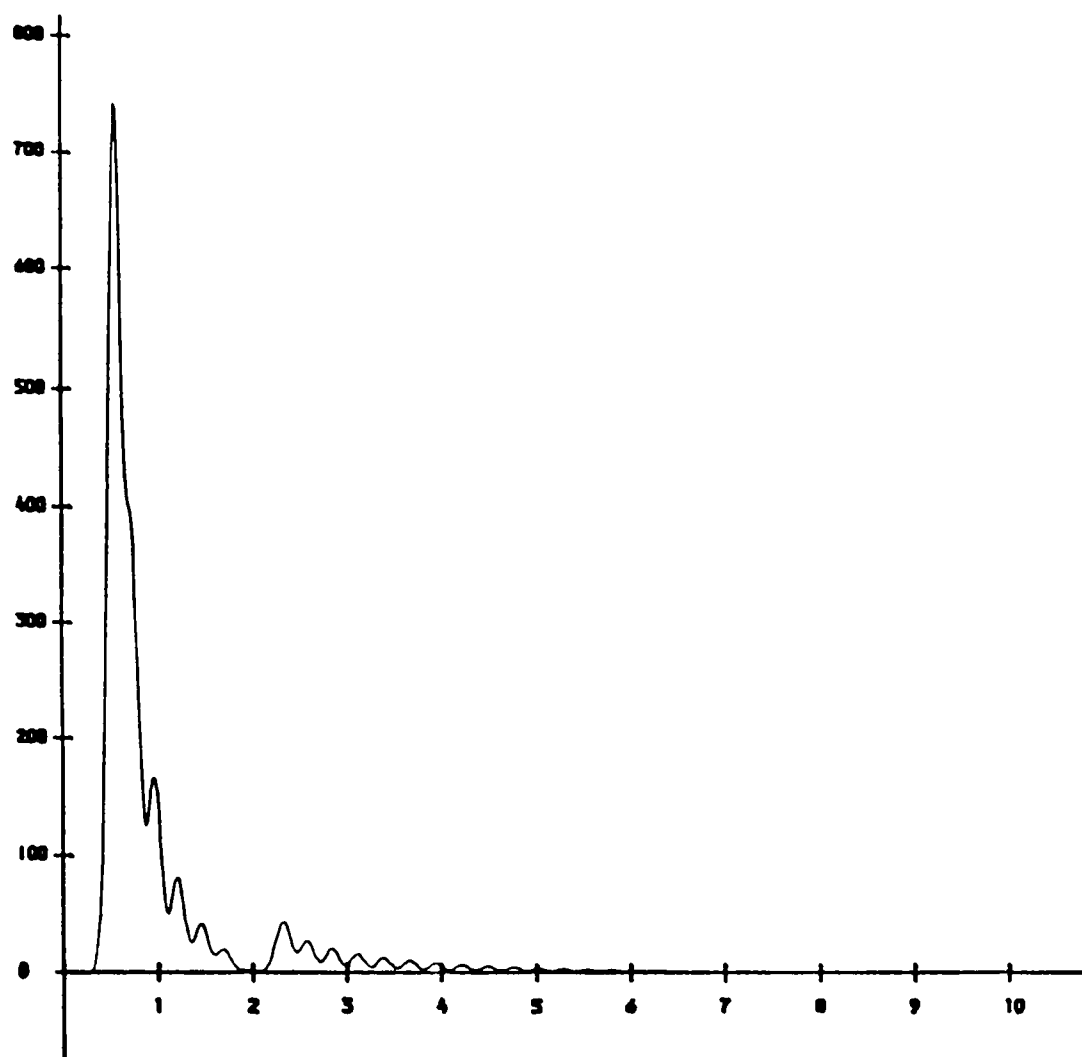


Fig. 2.25 Absorption of t-PA with six electrons removed. The soliton absorption now forms a broad band, responsible for virtually all of the absorption.

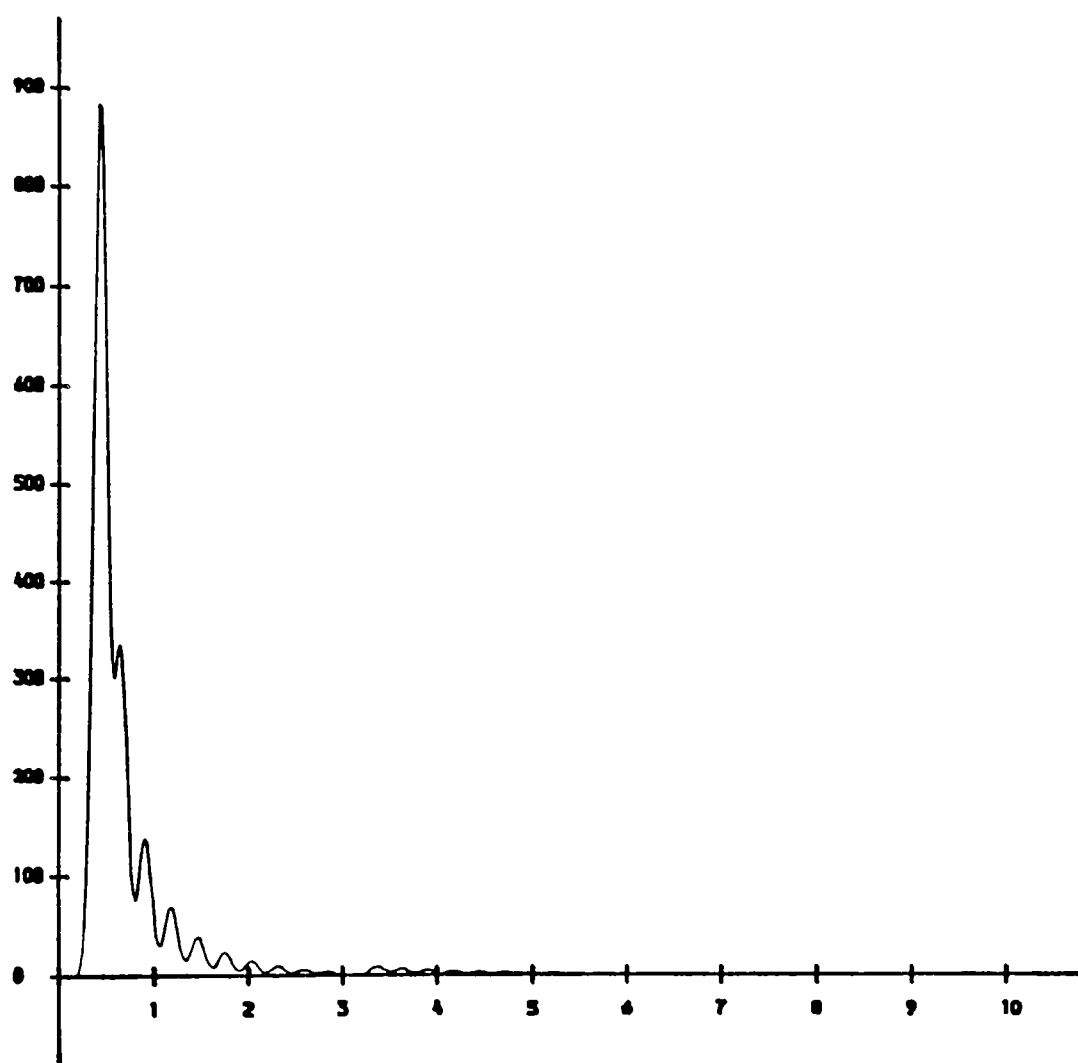


Fig. 2.26 Absorption of t-PA with ten electrons removed.

3.1 INTRODUCTION

The first three sections in this chapter derive results within the SSH Hamiltonian. Its treatment of the electron-lattice coupling can be used not only to derive self-consistent ground states for charged and uncharged chains but also to show how the phonon frequencies in t-PA (and, in principle, the non-degenerate polymers) are affected by being coupled to the electrons. Entirely numerical calculations of the phonon frequencies in a ground state chain have been performed before (Chao and Wang 1985), but these calculations are extremely costly and would be unsuitable for examining, for example, how the LO phonon frequency would vary with the empirical parameters used. Here the SSH wave functions, which have been calculated exactly, are used to derive phonon frequencies in terms of a series of integrals, with the n 'th integral representing the effective coupling between n 'th nearest neighbours. In the case of no dimerisation (§3.2), these integrals can be evaluated analytically and decay slowly with n , leading to a soft LO mode; dimerisation increases the rate at which the integrals decay and the LO mode takes finite frequency (§3.3).

Section 3.4 is concerned with calculating the constant C , which was introduced into the SSH Hamiltonian in §2.1 to prevent instability. Like the phonon frequencies, it can be calculated from the SSH eigenfunctions, in this case in terms of a pair of elliptic integrals, rather more economically than in the numerical manner of Stafström and Chao (1984a,b).

In section 3.5, the application of the SSH model to non-degenerate polymers is considered. In section 2.4, the method used was an *a priori* reasonable one of adding a term in the energy proportional to the dimerisation parameter, but other authors who have considered this problem (most notably Fesser *et al.* 1983) used a term which they added directly to the staggered displacement $\tilde{u}$. These two methods are shown to be equivalent, and the

numerical parameters involved are compared.

Sections 3.6 and 3.7 are concerned with the extension of the SSH Hamiltonian to include some treatment of electron-electron interaction. The application of the Hubbard U model is investigated, and its predictions for the absorption profiles of conjugated polymers are outlined and used to derive quantitative estimates of the strength of the interaction. The failure of this model to account for the anomalous strengths of individual photoinduced absorption peaks (as mentioned in §2.5) is explained in terms of its failure to break the charge conjugation symmetry of the SSH model.

3.2 ANALYTIC PHONON FREQUENCIES IN POLYACETYLENE

The method used here is based on that of Chao and Wang (1985), who wrote the time-dependent SSH Hamiltonian as:

$$H = H_{ST} + H_{PH} + H_{EP}$$

where H_{ST} , H_{PH} , and H_{EP} are the static, phonon and electron-phonon coupling terms in the total SSH Hamiltonian, given by:

$$H_{ST} = - \sum_{ns} (t_0 - \alpha(u_{n+1}^0 - u_n^0)) [c_{n+1,s}^+ c_{ns} + c_{ns}^+ c_{n+1,s}] \\ + \frac{1}{2} K \sum_n (u_{n+1}^0 - u_n^0 + C)^2$$

$$H_{EP} = \alpha \sum_{ns} (x_{n+1} - x_n) [c_{n+1,s}^+ c_{ns} + c_{ns}^+ c_{n+1,s}]$$

$$H_{PH} = K \sum_n (x_{n+1} - x_n) (u_{n+1}^0 - u_n^0 + C) \\ + \frac{1}{2} K \sum_n (x_{n+1} - x_n)^2 + \frac{1}{2} M \sum_n \dot{x}_n^2$$

Here the atomic displacements $\{u_n\}$ have been written in terms of their equilibrium values $\{u_n^0\}$ and displacements from equilibrium $\{x_n\}$.

H_{EP} is treated as a perturbation on the electronic Hamiltonian. The first order correction cancels the linear term in H_{PH} (this is the condition for the chain to be in equilibrium at $u_n = u_n^0$), and the second order correction gives the changes we must make to the calculated phonon frequencies.

The change in energy due to this second-order correction is given by:

$$\Delta E = \sum_{\Phi \neq \Psi} \frac{|\langle \Phi | H_{EP} | \Psi \rangle|^2}{E(\Phi) - E(\Psi)}$$

where $|\Psi\rangle$ is the ground state. If we write H_{EP} in terms of the one-electron eigenfunctions $\{|k\rangle\}$ in the same way as in §2.2, we get:

$$H_{EP} = \alpha \sum_{n,s} \sum_{k,\kappa} (x_{n+1} - x_n) (a_{n+1,k}^* a_{n\kappa} + a_{n\kappa}^* a_{n+1,\kappa}) c_{ks}^\dagger c_{\kappa s}$$

From orthogonality, we can ignore all $|\Phi\rangle$ except those with just one electron in a different (one-electron) eigenstate. In this case:

$$\langle \Phi | H_{EP} | \Psi \rangle = \alpha \sum_n (x_{n+1} - x_n) (a_{n+1,k}^* a_{n\kappa} + a_{n\kappa}^* a_{n+1,\kappa})$$

$$\text{so } \Delta E \approx \alpha^2 \sum_{k,\kappa} \sum_{n,m} (x_{n+1} - x_n) (a_{n+1,k}^* a_{n\kappa} + a_{n\kappa}^* a_{n+1,\kappa}) \cdot (x_{m+1} - x_m) (a_{m+1,k}^* a_{m\kappa} + a_{m\kappa}^* a_{m+1,\kappa})^* \cdot (E(\kappa) - E(k))^{-1}$$

(The sums over k and κ run over unoccupied and occupied states respectively.)

We can rewrite this sum as:

$$\begin{aligned} \Delta E \approx \alpha^2 \sum_{k,\kappa} \sum_{n,m} x_n x_m & (a_{n\kappa}^* a_{n-1,\kappa} + a_{n-1,k}^* a_{n\kappa} - a_{n+1,k}^* a_{n\kappa} - a_{n\kappa}^* a_{n+1,\kappa}) \cdot \\ & (a_{m\kappa}^* a_{m-1,\kappa} + a_{m-1,k}^* a_{m\kappa} - a_{m+1,k}^* a_{m\kappa} - a_{m\kappa}^* a_{m+1,\kappa})^* \cdot \\ & (E(\kappa) - E(k))^{-1} \end{aligned} \quad (3.1)$$

This was as far as Chao and Wang went in the analytic part of their calculations; they used the numerical wave functions to calculate $\partial^2 E / \partial x_n \partial x_m$ and hence the phonon frequencies, but it can be seen that this is an immensely time-consuming method, requiring $O(N^4)$ calculations due to the quadruple summation. For a uniformly dimerised chain, this number can be reduced dramatically (as will be shown in the next section); for an undimerised chain all of the summations above can be performed analytically as integrals, and this process is outlined here.

If we make the substitution $a_{nk} = e^{inka}/\sqrt{N}$, the last equation becomes (after multiplying out):

$$\Delta E \approx \alpha^2 / N^2 \sum_{k,\kappa} \sum_{n,m} x_n x_m e^{i(m-n)(k-\kappa)a} 4(\sin ka - \sin \kappa a)^2 \cdot (E(\kappa) - E(k))^{-1}$$

We can now make the following changes:

- (i) Replace $\sum_{\kappa}$ and $\sum_k$ by $\int_{-\pi/2a}^{\pi/2a} (a/2\pi) d\kappa$ and $\int_{\pi/2a}^{3\pi/2a} (a/2\pi) dk$ respectively
- (ii) Put $k' = k \pm \pi/a$, so $\sin ka = -\sin k'a$ and $\cos ka = -\cos k'a$
- (iii) Put $j = m-n$, as only the distance between atoms will affect the coupling.
- (iv) Replace the summation over spin states by a simple factor of 2.
- (v) Put $E(k) = -2t_0 \cos ka$.

These changes then give:

$$\Delta E \approx \frac{\alpha^2}{N^2} \left[\frac{Na}{2\pi} \right]^2 \int_{-\pi/2a}^{\pi/2a} dk' \int_{-\pi/2a}^{\pi/2a} d\kappa \sum_{nj} 2 \sum_{\Sigma} x_n x_{n+j} e^{ij(k'-\kappa-\pi/a)}.$$

$$4 (\sin k'a + \sin \kappa a)^2 \cdot (-2t_0 (\cos \kappa a + \cos k'a))^{-1}$$

$$\equiv \sum_{nj} V(j) x_n x_{n+j}$$

with:

$$V(j) = -\frac{\alpha^2}{t_0 \pi^2} e^{ij\pi} \int_{-\pi/2}^{\pi/2} d(k'a) \int_{-\pi/2}^{\pi/2} d(\kappa a) e^{ij(k'-\kappa)a}.$$

$$\left[2 \sin \frac{k'a + \kappa a}{2} \cos \frac{k'a - \kappa a}{2} \right]^2 \left[2 \cos \frac{\kappa a + k'a}{2} \cos \frac{k'a - \kappa a}{2} \right]^{-1}$$

With the final substitutions $\theta = (k'+\kappa)a$ and $\varphi = (k'-\kappa)a$, we get the much simpler form:

$$V(j) = -\frac{\alpha^2}{t_0 \pi^2} e^{ij\pi} \int_{-\pi}^{\pi} d\theta \int_{-\pi+|\theta|}^{\pi-|\theta|} d\varphi e^{ij\varphi} \frac{\sin^2 \theta/2 \cos \varphi/2}{\cos \theta/2}$$

We can integrate over φ without difficulty; let this integral be I_j :

$$I_j = \int_{-\pi+|\theta|}^{\pi-|\theta|} d\varphi e^{ij\varphi} \cos \varphi/2$$

$$= \frac{(-1)^{j+1}}{j^2 - \frac{1}{4}} \{2j \sin(|\theta|/2) \sin(j|\theta|) + \cos(|\theta|/2) \cos(j|\theta|)\}$$

The resulting integrand in θ is clearly even, so we change the limits and get:

$$V(j) = \frac{(-1)^{j+1} \alpha^2}{t_0 \pi^2 (j^2 - \frac{1}{4})} \int_0^{\pi} d\theta \{2j \sin(\theta/2) \sin(j\theta) + \cos(\theta/2) \cos(j\theta)\}.$$

$$\sin(\theta/2) \tan(\theta/2)$$

Now $\cos \theta/2 \sin \theta/2 \tan \theta/2 = \sin^2 \theta/2 = \frac{1}{2}(1 - \cos \theta)$ so the second term in the integral will vanish unless $j=0$ or 1 , due to the orthogonality of $\{\cos n\theta\}$ over the range 0 to π . Treating these two cases first:

$$V(0) = \frac{-8\alpha^2}{t_0\pi^2} \int_0^\pi d\theta \sin^2 \theta/2 = \frac{-4\alpha^2}{t_0\pi}$$

$$\begin{aligned} V(1) &= \frac{8\alpha^2}{3t_0\pi^2} \int_0^\pi d\theta \{2\sin \theta/2 \sin \theta + \cos \theta/2 \cos \theta\} \sin \theta/2 \tan \theta/2 \\ &= \frac{10\alpha^2}{3t_0\pi} \end{aligned}$$

$$\begin{aligned} \text{Also note that } & \int_0^\pi \sin^2 \theta/2 \sin j\theta \tan \theta/2 d\theta \\ &= \int_0^\pi \sin j\theta \tan \theta/2 - \frac{1}{2} \sin \theta \sin j\theta d\theta \\ &= \int_0^\pi \sin j\theta \tan \theta/2 d\theta \quad \text{if } j \neq 1 \quad (\text{orthogonality again}) \end{aligned}$$

Hence (for $j > 1$):

$$V(j) = \frac{4\alpha^2 j}{t_0\pi^2(j^2 - \frac{1}{4})} \int_0^\pi \sin j\theta \tan \theta/2 d\theta$$

This is evaluated by a recurrence relation for the integral itself (call it I'_j), which gives $I'_j = -I'_{j-1}$ ($j \geq 2$). Also $I'_1 = \pi$, so:

$$V(j) = \frac{4\alpha^2 j}{t_0\pi(j^2 - \frac{1}{4})} (-1)^{j+1} \quad (j \geq 2)$$

The overall effective phonon Hamiltonian is:

$$\begin{aligned} H_{PH}^{EFF} &= \frac{1}{2} K \sum_n (x_{n+1} - x_n)^2 + \sum_{nj} V(j) x_n x_{n+j} + \frac{1}{2} M \sum_n x_n^2 \\ &= \sum_{nj} V'(j) x_n x_{n+j} + \frac{1}{2} M \sum_n x_n^2 \end{aligned}$$

$$\begin{aligned} \text{where } V'(j) &= K - \frac{4\alpha^2}{t_0\pi} \quad (j=0) \\ &\quad - \frac{1}{2} K + \frac{10\alpha^2}{3t_0\pi} \quad (j=\pm 1) \\ &\quad \frac{4\alpha^2 j}{t_0\pi(j^2 - \frac{1}{4})} (-1)^{j+1} \quad (|j| \geq 2) \end{aligned}$$

Fesser, Bishop and Campbell (FBC) (1983) expressed the strength of electron-phonon coupling in terms of a dimensionless parameter λ , given by $\lambda = 2\alpha^2/K\pi at_0$, and in terms of $\Lambda (= \lambda a)$, the dispersion relation becomes:

$$\frac{M\omega^2}{K} = 2(1-2\Lambda) - 2(1-10\Lambda/3)\cos ka + \sum_{j=2}^{\infty} \frac{8\Lambda j}{(j^2-4)} (-1)^{j+1} \cos(jka) \quad (3.2)$$

There are three points to note:

- (i) If $\Lambda=0$, we have the classical result $\omega=(K/M)^{1/2} \cdot 2\sin(ka/2)$.
- (ii) At $k=0$, the sum over j becomes $-8\Lambda/3$, giving $\omega=0$ as expected.
- (iii) At $k=\pi/a$, the sum over j diverges and the R.H.S. becomes large and negative for $\Lambda \neq 0$. This is also expected - it indicates that there is a soft phonon, in other words that the system is unstable with respect to dimerisation.

3.3 DIMERISATION AND PHONON FREQUENCIES

To find the phonon frequencies in the dimerised state, all we need do is use the appropriate eigenfunctions in equation (3.1) above (p.3.3). These eigenfunctions were given by SSH (wrongly in their original paper, but the mistake was corrected in the *erratum*):

$$a_{nk} = (2N)^{-1/2} \{ e^{ikna} \cdot \Gamma_k^- \pm i \operatorname{sgn}(k) e^{i(k+\pi/a)na} \cdot \Gamma_k^+ \}$$

where the + sign applies in the conduction band and the - in the valence band; Γ_k^+ and E_k are given by:

$$\Gamma_k^+ = \left[1 \pm \frac{2t_0 \cos ka}{E_k} \right]^{1/2}, \quad E_k^2 = (2t_0 \cos ka)^2 + (4\alpha u_0 \sin ka)^2$$

E_k is of opposite sign to $\cos ka$, so as $\alpha u_0 \rightarrow 0$, $\Gamma_k^+ \rightarrow 0$ and $\Gamma_k^- \rightarrow \sqrt{2}$, which gives the undimerised result $a_{nk} = e^{ikna}/\sqrt{N}$. Equation (3.1) involves summation over k in the conduction band and κ in the valence band, so the $\{a_{nk}\}$ will use the + sign and the $\{a_{n\kappa}\}$ the - sign. This leads to the following rather complicated expression for the second order change in energy:

$$\Delta E = \alpha^2 \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{\mathbf{n}} \sum_{\mathbf{m}} x_{\mathbf{n}} x_{\mathbf{m}} \cdot \frac{1}{N^2} e^{-i(\mathbf{k}-\mathbf{k}')(\mathbf{n}-\mathbf{m})\mathbf{a}} \{E(\mathbf{k}') - E(\mathbf{k})\}^{-1}.$$

$$\begin{aligned} & \left\{ [\Gamma_{\mathbf{k}}^- \Gamma_{\mathbf{k}'}^- + \text{sgn}(\mathbf{k}\mathbf{k}') \Gamma_{\mathbf{k}}^+ \Gamma_{\mathbf{k}'}^+]^2 [\sin \mathbf{k}\mathbf{a} - \sin \mathbf{k}'\mathbf{a}]^2 \right. \\ & + (-1)^{n+m} [\text{sgn}(\mathbf{k}) \Gamma_{\mathbf{k}}^+ \Gamma_{\mathbf{k}'}^- - \text{sgn}(\mathbf{k}') \Gamma_{\mathbf{k}}^- \Gamma_{\mathbf{k}'}^+]^2 [\sin \mathbf{k}\mathbf{a} + \sin \mathbf{k}'\mathbf{a}]^2 \\ & + [\Gamma_{\mathbf{k}}^- \Gamma_{\mathbf{k}'}^- + \text{sgn}(\mathbf{k}\mathbf{k}') \Gamma_{\mathbf{k}}^+ \Gamma_{\mathbf{k}'}^+] [\text{sgn}(\mathbf{k}) \Gamma_{\mathbf{k}}^- \Gamma_{\mathbf{k}'}^+ - \text{sgn}(\mathbf{k}') \Gamma_{\mathbf{k}}^+ \Gamma_{\mathbf{k}'}^-] \\ & \left. [\sin \mathbf{k}\mathbf{a} - \sin \mathbf{k}'\mathbf{a}] [\sin \mathbf{k}\mathbf{a} + \sin \mathbf{k}'\mathbf{a}] [(-1)^m - (-1)^n] \right\} \end{aligned}$$

If we convert the summations to integrals in the same manner as in the previous section, we have the following expression for the $\{V_{mn}\}$:

$$V_{mn} = \frac{\alpha^2}{2\pi^2} \{(-1)^{n-m} V_1 + V_2 + [(-1)^m - (-1)^n] V_3\} \quad (3.3)$$

$$\begin{aligned} \text{where } V_1 &= \int_{-\pi/2}^{\pi/2} d(\mathbf{k}'\mathbf{a}) \int_{-\pi/2}^{\pi/2} d(\mathbf{k}\mathbf{a}) \cos[(\mathbf{k}' - \mathbf{k})(\mathbf{n} - \mathbf{m})\mathbf{a}] \cdot [E(\mathbf{k}) + E(\mathbf{k}')]^{-1} \\ & \quad [\Gamma_{\mathbf{k}}^-, \Gamma_{\mathbf{k}'}^- - \text{sgn}(\mathbf{k}'\mathbf{k}) \Gamma_{\mathbf{k}}^+, \Gamma_{\mathbf{k}'}^+]^2 [\sin \mathbf{k}\mathbf{a} + \sin \mathbf{k}'\mathbf{a}]^2 \\ V_2 &= \int_{-\pi/2}^{\pi/2} d(\mathbf{k}'\mathbf{a}) \int_{-\pi/2}^{\pi/2} d(\mathbf{k}\mathbf{a}) \cos[(\mathbf{k}' - \mathbf{k})(\mathbf{n} - \mathbf{m})\mathbf{a}] \cdot [E(\mathbf{k}) + E(\mathbf{k}')]^{-1} \\ & \quad [\text{sgn}(\mathbf{k}') \Gamma_{\mathbf{k}}^+, \Gamma_{\mathbf{k}'}^- + \text{sgn}(\mathbf{k}) \Gamma_{\mathbf{k}}^-, \Gamma_{\mathbf{k}'}^+]^2 [\sin \mathbf{k}\mathbf{a} - \sin \mathbf{k}'\mathbf{a}]^2 \\ V_3 &= \int_{-\pi/2}^{\pi/2} d(\mathbf{k}'\mathbf{a}) \int_{-\pi/2}^{\pi/2} d(\mathbf{k}\mathbf{a}) \sin[(\mathbf{k}' - \mathbf{k})(\mathbf{n} - \mathbf{m})\mathbf{a}] \cdot [E(\mathbf{k}) + E(\mathbf{k}')]^{-1} \\ & \quad [\Gamma_{\mathbf{k}}^-, \Gamma_{\mathbf{k}'}^- - \text{sgn}(\mathbf{k}'\mathbf{k}) \Gamma_{\mathbf{k}}^+, \Gamma_{\mathbf{k}'}^+] [\text{sgn}(\mathbf{k}') \Gamma_{\mathbf{k}}^+, \Gamma_{\mathbf{k}'}^- + \text{sgn}(\mathbf{k}) \Gamma_{\mathbf{k}}^-, \Gamma_{\mathbf{k}'}^+] \\ & \quad [\sin^2 \mathbf{k}\mathbf{a} - \sin^2 \mathbf{k}'\mathbf{a}] \end{aligned}$$

The "genuine" potential energy term $V = \frac{1}{2} K \sum_{\mathbf{n}} (x_{\mathbf{n}+1} - x_{\mathbf{n}})^2$ gives additional matrix elements:

$$V_{mm} = K \quad V_{m, m \pm 1} = -\frac{1}{2} K$$

and this leads to the following total matrix elements (again expressed in terms of a separation j):

$$\begin{aligned} V(0) &= K + \frac{\alpha^2}{2\pi^2} \{V_1(0) + V_2(0)\} \\ V(1) &= -\frac{1}{2} K + \frac{\alpha^2}{2\pi^2} \{-V_1(1) + V_2(1) \pm 2V_3(1)\} \\ V(2n) &= \frac{\alpha^2}{2\pi^2} \{V_1(2n) + V_2(2n)\} \end{aligned}$$

$$V(2n+1) = \frac{\alpha^2}{2\pi^2} \{-V_1(2n+1)+V_2(2n+1)\pm 2V_3(2n+1)\}$$

where the $\pm$ sign is + if m is even, n is odd and $n>m$, or if m is odd, n even and $m>n$.

If we now write down the resulting dispersion relation, we get:

$$M\omega^2 = 2 [A_0+2A_2\cos 2ka+2A_4\cos 4ka+\dots] \pm 4 [(A_1\cos ka+A_3\cos 3ka+\dots)^2+(B_1\sin ka+B_3\sin 3ka+\dots)^2]^{\frac{1}{2}} \quad (3.4)$$

where $A_0 = V(0)$

$$A_1 = -\frac{1}{2} K + \frac{\alpha^2}{2\pi^2} \{-V_1(1)+V_2(1)\}$$

$$A_n = \frac{\alpha^2}{2\pi^2} \{(-1)^n V_1(n)+V_2(n)\} \quad (n \geq 2)$$

$$B_n = \frac{\alpha^2}{\pi^2} V_3(n) \quad (n \text{ odd})$$

The integrals must be calculated numerically, but there remains a substantial advantage over the method of Chao and Wang in the time taken; Chao and Wang require $O(N^4)$ evaluations, whereas this method needs only $O(N^2)$.

The effect of dimerisation on the phonon frequencies is shown in figs. 3.1-3.3; the frequencies are plotted in units of $(K/M)^{\frac{1}{2}}$, which is approximately 950cm^{-1} using the parameters of §2.1 (the values used by SSH give rather lower frequencies, due to their underestimating the spring constant K). Thus the frequency calculated by ignoring electron-phonon coupling (the *bare frequency*) would be 1900cm^{-1} . The LO phonon frequency in the dimerised state (fig. 3.3) is calculated to be $1.34(K/M)^{\frac{1}{2}}$, or about 1270cm^{-1} . The interactions were summed over 100 neighbours on each side, and in the undimerised case (fig. 3.2) the oscillation in ω is a sign that long-range forces are at work. How the range of these forces is reduced by dimerisation is shown in figs. 3.4 and 3.5. Fig. 3.4 shows $V_1(n)$ (actually $-V_1(n)$) plotted against n for various levels of dimerisation, expressed in terms of the dimensionless variable z ($= 2\alpha u_0/t_0$), which is directly

observed to be 0.14. While V_1 remains the dominant term even for $z > 0$, the coupling really depends on $V_1(n) + (-1)^n V_2(n)$, and this is plotted in fig. 3.5.

The Chao and Wang model assumes that the electronic wavefunctions (or rather the coefficients of each atomic orbital in the molecular wavefunctions) do not change during the nuclear motion. If we go to the opposite extreme (essentially, make the Born-Oppenheimer approximation), we can derive a frequency for the $k=0$ optic mode just by evaluating the second derivative of the total energy curve given by the SSH model (and drawn in fig. 1.2). This is a trivial calculation to perform, and gives a frequency (using the same parameters) $\omega = 1.28(K/M)^{1/2}$. This is very close to the frequency derived within the Chao and Wang model ($\omega = 1.34(K/M)^{1/2}$), and on the "correct" side (the frequency corresponding to complete relaxation of the electrons must be less than any other frequency we calculate).

Experimental values of the Raman frequencies of polyacetylene have been obtained by Lefrant *et al.* (1979), and a Raman-active absorption is observed at 1470cm^{-1} . The fact that the method used here gives $\omega = 1270\text{cm}^{-1}$ may mean that we have slightly overestimated the effect of electron-phonon coupling; however, the calculated frequency is very sensitive to the initial parameters used in the SSH model. Changing the overlap integral t_0 to 3eV (which, on looking at the original results of Grant and Batra (1979), is perhaps a better approximation than the 2.5eV used normally) would appear to reduce λ by a factor 5/6 immediately, bringing the calculated frequency up to 1380cm^{-1} , although the situation is not as simple as this, of course, and a complete recalculation of the ground state geometry should be carried out before results can be quoted with any degree of confidence.

Mele and Rice (1980) calculated Raman frequencies in a force field model with and without electron-phonon coupling, choosing their coupling parameter to optimise the fit to experimental data. Their value for the

bare frequency was 1900 cm^{-1} , as above, and they calculated the coupled frequency to be 1487 cm^{-1} . However, the coupling parameter they obtained does appear rather low - even using an overlap integral $t_0=3\text{eV}$, they only predicted a band gap of 1.3eV (if anything, the standard value of 1.4eV is itself possibly an underestimate).

3.4 DIMERISATION AND THE EQUILIBRIUM LENGTH

As explained in §2.1, the SSH Hamiltonian, as initially proposed, leads to a chain unstable with respect to global contraction, since the electron-phonon coupling term gives a negative energy linear in atomic displacement, while the potential energy term is positive and quadratic. To overcome the difficulties that this causes to self-consistent calculations, an extra parameter has to be included in the potential energy term to shift the energy minimum. This is the parameter C which was introduced in §2.1, and which leads to the modified Hamiltonian:

$$H = - \sum_n (t_0 - \alpha(u_{n+1} - u_n)) [c_{n+1}^+ c_n + c_n^+ c_{n+1}] \\ + \frac{1}{2} K \sum_n (u_{n+1} - u_n + C)^2$$

When numerically relaxing a polyacetylene chain it is useful to know the correct value of C for the dimerised chain. Stafstrom and Chao (1984a) assumed that it was unchanged from its value in undimerised polyacetylene, and here we find the extent of the error in this assumption.

On solving for self-consistency in a dimerised chain, the condition that there be no global contraction or expansion in the ground state is equivalent to the requirement that $u_n = u_{n+2}$ for all n , giving:

$$C = \frac{-\alpha}{2K} \sum_{kn} (a_{n+1,k}^* a_{nk} + a_{nk}^* a_{n+1,k})$$

where k is summed over all occupied states and $n=1,2$.

Using the same notation as in §§3.2 and 3.3, the bracket becomes:

$$(2N)^{-1} \{ [(\Gamma_k^-)^2 - (\Gamma_k^+)^2] \cdot 2\cos ka + 4\Gamma_k^- \Gamma_k^+ (-1)^n \text{sgn}(k) \sin ka \} \\ = (-8t_0^2 \cos^2 ka - 16\alpha u_0 (-1)^n \sin^2 ka) / 2NE_k$$

since $(\Gamma_k^-)^2 - (\Gamma_k^+)^2 = -4t_0 \cos ka / E_k$ and $\Gamma_k^- \Gamma_k^+ = 4\alpha u_0 |\sin ka / E_k|$.

The second term will cancel on summation over n , leaving:

$$C = \frac{\alpha}{KN} \sum_k 4t_0 \cos^2 ka / E_k$$

with $E_k^2 = (2t_0 \cos ka)^2 + (4\alpha u_0 \sin ka)^2$ as before. On replacing the sum by an integral, with $z = 2\alpha u_0 / t_0$, we get:

$$\begin{aligned} C &= \frac{-4\alpha}{\pi K} \int_0^{\pi/2} \frac{\cos^2 \theta d\theta}{(1 - (1-z^2)\sin^2 \theta)^{\frac{1}{2}}} \\ &= \frac{-4\alpha}{\pi K} \left[\frac{-z^2}{(1-z^2)} K(1-z^2) + \frac{1}{(1-z^2)} E(1-z^2) \right] \end{aligned}$$

where K and E are complete elliptic integrals of the first and second kinds respectively. It is trivial to see that the $z \rightarrow 0$ limit leads to the correct value of $C = -4\alpha / K\pi$ for the undimerised chain.

For small z , we use the approximations (Abramovitz & Stegun 1965):

$$K(1-z^2) \approx \frac{1}{2} \ln(16/z^2)$$

$$E(1-z^2) \approx 1 + 0.463z^2 + 0.245z^2 \ln(1/z^2)$$

whereupon:

$$C \approx -4\alpha / K\pi \{ 1 + 0.08z^2 + 0.255z^2 \ln(z^2) \}$$

For polyacetylene, with $z^2 \approx 0.02$, this gives $C = -1.250 \alpha / K$. The undimerised value is -1.273 and Stafström and Chao found -1.250 numerically, wrongly attributing the difference to the fact that they were using a discrete system rather than a continuous one.

3.5 TWO METHODS OF TREATING NON-DEGENERACY IN THE GROUND STATE

Fesser, Bishop and Campbell (FBC) (1983), as well as other authors, have used a direct change in the dimerisation parameter $\tilde{u}$ (or the proportional quantity Δ) to model polymers with a non-degenerate ground state. This method is equivalent to the *a priori* method of adding a term in the energy proportional to u that was used in chapter 2, as is shown below.

Take the SSH Hamiltonian, modified to take account of the absence of ground state degeneracy:

$$H = - \sum_n (t_0 - \alpha(u_{n+1} - u_n)) [c_{n+1}^+ c_n + c_n^+ c_{n+1}] \\ + \frac{1}{2} K \sum_n (u_{n+1} - u_n - C)^2 + S \sum_n (-1)^n u_n$$

and write the lattice displacements as $u_n = u_n^0 + u^i(-1)^n$, where u^i is a constant (at this stage, purely arbitrary). We are, of course, perfectly free to write u_n in any way we choose. The Hamiltonian now becomes:

$$H = H_{el}(\{u_n\}) + \frac{1}{2} K \left[\sum_n (u_{n+1}^0 - u_n^0 - C)^2 + 4N(u^i)^2 \right. \\ \left. + 8u^i \sum_n u_n^0 \right] + S \sum_n ((-1)^n u_n^0 + u^i)$$

If we now choose to consider the special case $u^i = -S/4K$, this becomes:

$$H = H_{el}(\{u_n\}) + \frac{1}{2} K \sum_n (u_{n+1}^0 - u_n^0 - C)^2 + \text{constant}$$

This takes the form of the electronic Hamiltonian in terms of the $\{u_n\}$, and the potential energy contribution in terms of the $\{u_n^0\}$. In addition, the system it describes does not have a degenerate ground state (unless $u^i=0$). FBC started with the assumption that the Hamiltonian due to Takayama, Lin-Liu and Maki (TLM) (1980) could be modified to take account of ground state non-degeneracy by adding a constant to $\tilde{u}$, and derived an equivalent result.

Now that we have shown these two methods to be equivalent, we can compare the *steric parameter* used previously to model cis-polyacetylene with FBC's *confinement parameter*. The latter was given by:

$$\gamma = \Delta_e / \lambda \Delta_0 = u^i / \lambda u_0 \quad \text{with} \quad \lambda = 2\alpha^2 / K\pi\alpha t_0$$

so we can relate the two parameters by $\gamma = S\pi\alpha t_0 / 8u_0\alpha^2$.

In c-PA, we found that $S = 1.0\text{eV}\text{\AA}^{-1}$ gave a good fit to the band gap (§2.4). Using this value, we obtained $u_0 \approx 0.03L$, so $\gamma \approx 0.7$; this is in good agreement with FBC's estimate that γ lies between 0.5 and 1.0, an estimate derived from approximate quantum chemical calculations.

3.6 CHARGE CONJUGATION SYMMETRY AND ELECTRON-ELECTRON INTERACTION

In this section the SSH Hamiltonian, is modified to take some account of electron-electron interaction. The *Hubbard U* method is used (Hubbard 1963), and is able to account for the photoinduced absorption profiles of t-PA and polythiophene in terms of the positions of the absorption peaks. The question of the relative strengths of the absorption peaks (see §2.5) is unresolved, however, as the anomaly between observed absorption weights and those predicted within the SSH model is a consequence of the charge conjugation symmetry of the SSH Hamiltonian. This has been shown by Fesser *et al.* (1983), and the nature of charge conjugation symmetry (CCS) is discussed both in that paper and by Sum *et al.* (1988). It is not discussed in detail here, but a few of the results used below are consequences of CCS and a very brief outline of the symmetry is given here in order to explain their origins.

Consider the SSH Hamiltonian:

$$H = - \sum_n \sum_s (t_0 - \alpha(u_{n+1} - u_n)) [c_{n+1,s}^+ c_{ns} + c_{ns}^+ c_{n+1,s}] \\ + \frac{1}{2} K \sum_n (u_{n+1} - u_n - C)^2 + S \sum_n (-1)^n u_n$$

Using the fact that the anti-commutators are given by:

$$\{c_{n\sigma}^+, c_{ms}\} = \delta_{mn} \delta_{s\sigma} \quad \{c_{n\sigma}^+, c_{ms}^+\} = \{c_{n\sigma}, c_{ms}\} = 0,$$

it is easily seen that the Hamiltonian is invariant under the transformation $c_{ns}^+ \rightarrow (-1)^n c_{ns}$. Given that this transformation represents a method of interchanging electrons and holes, the resulting symmetry is known as *electron-hole*, or *charge conjugation* symmetry. Its immediate consequences are that electronic states must occur in pairs, symmetrically spaced about midgap, since an electronic wave function of energy ϵ is equivalent to a hole wave function of energy $-\epsilon$; the states have wave functions which transform into each other by means of the relation $a_{nk} \rightarrow (-1)^n a'_{nk}$. If the total number of states is constrained to be odd, by using a chain of odd length, these conditions dictate that the unpaired

state must lie at midgap and must have a zero component at each alternate site. Note that this result does not depend on the geometry of the chain; it applies not only to a soliton in the dimerised chain but also to the $k=\pi/2a$ eigenfunction in an undimerised chain.

The reason that luminescence quenching relies on violation of CCS is that the current operator, which in the SSH representation is proportional to $\sum (c_n^\dagger c_{n+1} - c_{n+1}^\dagger c_n)$ (Danielsen and Ball 1985), is odd under the CCS transformation. It follows that photoexcitation must result in an excited state of opposite parity to the ground state; since there is no term in the Hamiltonian which is capable of mixing states of different parity, the only means by which the photoexcited state can decay back to the ground state is via a radiative process, and luminescence is therefore predicted to be 100% efficient. However, a quantum yield of only about $10^{-3}\%$ is found (Lauchlan *et al.* 1981), and it is clear that CCS is being broken in some manner. The question of luminescence in c-PA is discussed further in chapter 7.

The *Hubbard U* method used to represent electron-electron interaction has been applied by a number of authors (for example Kivelson and Heim 1982, Stafstrom and Chao 1984b) to the case of conjugated polymers. An extra term is added to the Hamiltonian:

$$\begin{aligned} H_c &= U \sum (c_{n+}^\dagger c_{n+} - \frac{1}{2})(c_{n-}^\dagger c_{n-} - \frac{1}{2}) \\ &= U [\sum c_{n+}^\dagger c_{n+} c_{n-}^\dagger c_{n-} - \frac{1}{2} N_{e1} + \frac{1}{4} N] \end{aligned} \quad (3.5)$$

where N_{e1} and N are the numbers of electrons and atoms in the system respectively. It is easily seen that this model does not break CCS as long as the chain is uncharged, but the case of a charged chain is more complicated than it appears, since there are no longer equal numbers of electrons and holes in the chain. Sum *et al.* (1988) discussed the addition of a more general Hubbard-type model of electron-electron interaction to the SSH model, and advised caution when interpreting any results involving the breaking or otherwise of CCS. The results of this chapter all treat the electron-electron interaction as a first order perturbation on the SSH

results, so the question of CCS-breaking does not arise; much of the remainder of this thesis is concerned with the development of a method for treating conjugated polymers which does not display CCS and whose results should be more reliable.

To find the Coulomb contribution to the chain energy, we can write:

$$\sum_n c_{n+}^+ c_{n+} c_{n-}^+ c_{n-} = \sum_{n\kappa k} |a_{n\kappa+}|^2 |a_{n\kappa-}|^2 c_{\kappa+}^+ c_{\kappa+} c_{\kappa-}^+ c_{\kappa-}$$

where the suffix $\pm$ refers to a spin state. The change in energy is therefore (to first order):

$$\Delta E_c = U \left[\sum_{n\kappa k} |a_{n\kappa+}|^2 |a_{n\kappa-}|^2 - \frac{1}{2} N_e + \frac{1}{4} N \right]$$

The one-electron energy change in a state $|k+\rangle$ is:

$$\begin{aligned} \Delta \epsilon(k+) &= U \sum_n |a_{nk+}|^2 \left(\sum_{\kappa} |a_{n\kappa-}|^2 - \frac{1}{2} \right) \\ &= U \left(\sum_{n\kappa} |a_{nk+}|^2 |a_{n\kappa-}|^2 - \frac{1}{2} \right) \quad \text{as } \sum_n |a_{nk+}|^2 = 1 \end{aligned}$$

where all sums over k or κ are assumed to be taken over occupied states.

This result is used below to calculate the Coulomb energies of each of the possible defect types in a chain; the results apply equally to t-PA and to polymers without degeneracy in the ground state.

1. SOLITONS

A neutral soliton is charge neutral locally as well as globally (this is a consequence of CCS) so:

$$2 \sum_k |a_{nk}|^2 + |a_n^{\text{sol}i}|^2 = 1$$

Now consider the four possible solitons: S^+ , $S_{\frac{1}{2}}^0$, S^- , where the superfix represents the soliton charge and the suffix the soliton spin (the charged solitons are spinless). They have electron densities:

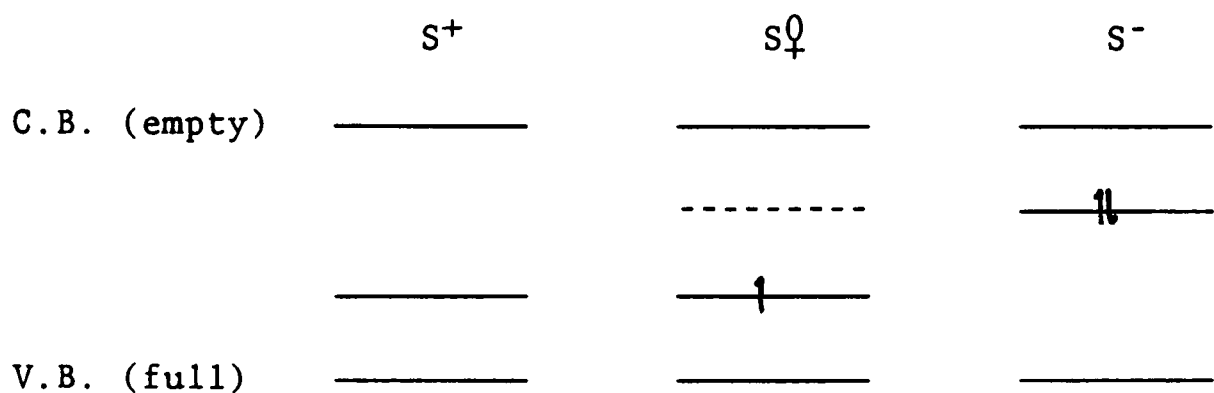
Spin	S^+	$S_{\frac{1}{2}}^0$	S^-
+	$\frac{1}{2}(1 - a_n^{\text{sol}i} ^2)$	$\frac{1}{2}(1 \pm a_n^{\text{sol}i} ^2)$	$\frac{1}{2}(1 + a_n^{\text{sol}i} ^2)$
-	$\frac{1}{2}(1 - a_n^{\text{sol}i} ^2)$	$\frac{1}{2}(1 \mp a_n^{\text{sol}i} ^2)$	$\frac{1}{2}(1 + a_n^{\text{sol}i} ^2)$

Hence the Coulomb energies of the solitons are:

$$\begin{aligned}\Delta E_c(S^\pm) &= U \left(\frac{1}{4} \sum (1 \mp |a_n^{\text{sol}}|^2)^2 - \frac{1}{2} (N \mp 1) + \frac{1}{4} N \right) \\ &= \frac{1}{4} U \sum |a_n^{\text{sol}}|^4 \quad \text{as } \sum |a_n^{\text{sol}}|^2 = 1 \\ \Delta E_c(S^0) &= -\frac{1}{4} U \sum |a_n^{\text{sol}}|^4 \quad \text{similarly.}\end{aligned}$$

Kivelson and Heim, writing U_{eff} for $U \sum |a_n^{\text{sol}}|^4$, obtain these results and mention that they can be explained in terms of the effective repulsion $\frac{1}{2} U_{\text{eff}}$ between localised states. Note that U_{eff} is reduced from U by a factor of order ℓ , where ℓ is the width of the soliton.

The one-electron energy levels are displaced by $\pm \frac{1}{2} U_{\text{eff}}$, with the $+$ sign if the localised state of the opposite spin is full, and the $-$ if it is empty, so the energy level diagrams become:



The band states only move slightly in energy; if we consider the effect of a charged soliton $S^\pm$ on a general state $|k+\rangle$, we have:

$$\begin{aligned}\Delta \epsilon(k+) &= U \left\{ \sum_{n\kappa} |a_{n\kappa-}|^2 |a_{n\kappa+}|^2 - \frac{1}{2} \right\} \\ &= \mp \frac{1}{2} U \sum |a_{n\kappa+}|^2 |a_n^{\text{sol}}|^2 \quad \text{which is } O(U/N) \text{ at most.}\end{aligned}$$

If we then sum all the one-electron energy changes, we get:

$$\sum \Delta \epsilon(k+) = \mp \frac{1}{2} U + \frac{1}{2} U \sum |a_n^{\text{sol}}|^4$$

where the first term represents removing an electron from (adding it to) the system and the second is the total Coulomb energy (double-counted of course) due to the soliton. Note that this second term is, as we would expect, twice the total energy change evaluated above. For a neutral soliton the equivalent term is $-\frac{1}{2} U \sum |a_n^{\text{sol}}|^4$.

2. POLARONS

As in the soliton case, CCS yields significant information about the defect wave functions; in this case the localised state wavefunctions are related by $a_n^{\text{hi}} = (-1)^n a_n^{\text{lo}}$, where the superfixes hi and lo refer to the higher and

lower polaron states. Thus $|a_n^{hi}|^2 = |a_n^{lo}|^2 \equiv |a_n^{pol}|^2$.

Excitons are locally charge neutral (CCS again), so for polarons (and this argument applies to bipolarons as well, of course), we have:

$$2 \sum |a_{nk}|^2 + 2|a_n^{pol}|^2 = 1$$

so $\sum |a_{nk}|^2 = \frac{1}{2} (1 - 2|a_n^{pol}|^2)$

A bipolaron has electron densities $\frac{1}{2} (1 \mp 2|a_n^{pol}|^2)$ in each spin, giving a Coulomb energy:

$$\begin{aligned} \Delta E_c &= \frac{1}{4} U \{ \sum (1 - 2|a_n^{pol}|^2)^2 - 2(N \mp 2) + N \} \\ &= U \sum |a_n^{pol}|^4 \end{aligned}$$

Polarons, however, have to first order no Coulomb energy, since the electron density in whichever spin has *not* had charge added is still $\frac{1}{2}$ throughout; that this leads trivially to a zero Coulomb energy is most easily seen by going back to the original expression (3.5) (p. 3.14).

3. EXCITONS

When we are concerned with photoexcited states, we will normally be considering excitons, rather than polarons or solitons. Excitons are analogous to bipolarons, but with one electron in each of the upper and lower polaron states; if Coulomb interactions are ignored, the energy levels are identical to those in the bipolaron (in trans-polyacetylene the bipolaron is unstable with respect to decay into two solitons, and the same applies, within the SSH model, to the exciton, as shown by Su and Schrieffer (1980)).

Excitons must be treated with more care than polarons or bipolarons, as we must make sure to preserve the correct antisymmetric wavefunctions (this is only necessary in this case, since excitons are the only states with two unpaired electrons). For the singlet exciton we have (Grabowski *et al.* 1985):

$$\Psi_s = 2^{-\frac{1}{2}} (c_{lo,+}^\dagger c_{hi,-}^\dagger + c_{hi,+}^\dagger c_{lo,-}^\dagger) |V\rangle$$

where $|V\rangle$ represents the (distorted) valence band. Working out the expectation value $\langle \Psi_s | H_c | \Psi_s \rangle$, we get four terms, of which only the two

cross terms actually contribute to the energy of the exciton. It should be noted that we have to use the unsimplified version of the Coulomb term expressed in terms of the eigenstates:

$$\sum_n c_n^+ c_n + c_n^+ c_n^- = \sum_{nk_1} \sum_{nk_2} \sum_{nk_3} \sum_{nk_4} a_{nk_1}^* a_{nk_2} + a_{nk_3}^* a_{nk_4} - c_{k_1}^+ c_{k_2} + c_{k_3}^+ c_{k_4} -$$

as it is no longer true that non-zero terms will only occur if $k_1=k_2$ and $k_3=k_4$. The resulting Coulomb energy is $U \sum |a_n^{pol}|^4$, perhaps a surprising result as it is unusual to see an exciton destabilised by Coulomb interaction.

The same mathematics applies for the triplet exciton, with the wavefunction now:

$$\Psi_t = 2^{-\frac{1}{2}} (c_{l_0,+}^+ c_{h_i,-}^+ - c_{h_i,+}^+ c_{l_0,-}^+) |V\rangle$$

and the Coulomb energy $-U \sum |a_n^{pol}|^4$. Although this is the lower energy state, it is unlikely often to be seen due to non-conservation of spin.

3.7 CHANGES TO ABSORPTION PROFILES

Here we consider the effect of Coulomb interaction on the positions of the absorption, particularly photo-induced absorption, lines in conjugated polymers (absorption due to dopant-induced defects is complicated by the Coulomb pinning between dopant and defect). If we find the change in energy due to the Hubbard U before and after the excitation process, we should be able to obtain the amount by which the absorption lines are shifted in this model. Note that we can virtually ignore any changes in the valence and conduction bands - only the occupancies of the localised states are important in determining the Coulomb energy.

We label the transitions as follows:

Soliton - (1) Valence band to localised state

(2) Localised state to conduction band

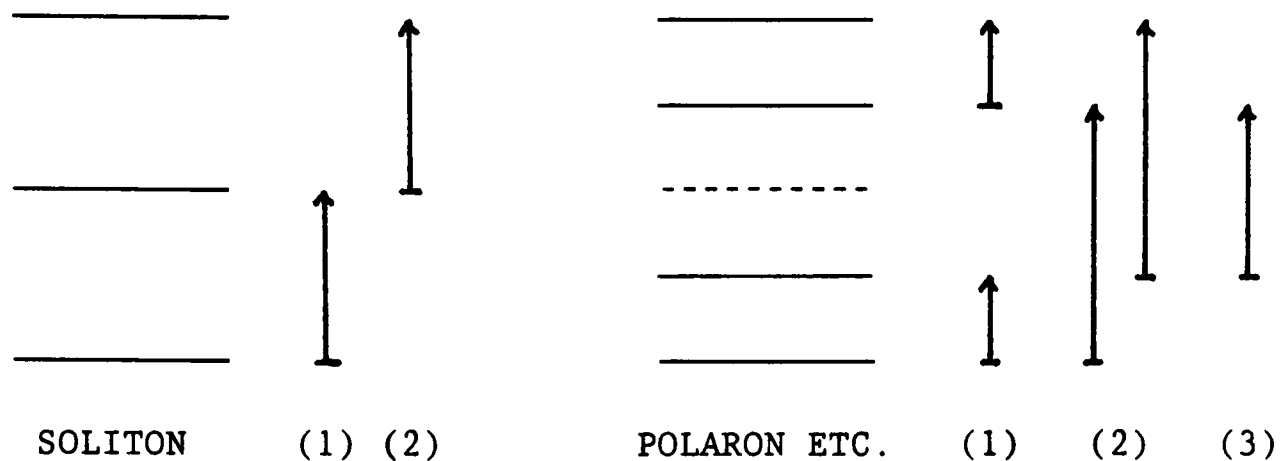
Polaron etc. - (1) Valence band to lower localised state, or

Higher localised state to conduction band

(2) Valence band to higher localised state, or

Lower localised state to conduction band

(3) Lower to higher localised state



Then we would expect the following energy changes:

NEUTRAL SOLITON: Both (1) and (2) create what is effectively a charged soliton, and so will be increased in energy by $\approx \frac{1}{2} U_{\text{eff}}$.

CHARGED SOLITON: Whichever of (1) and (2) is allowed will be decreased in energy by $\approx \frac{1}{2} U_{\text{eff}}$; even if we make sure that the wavefunction describing the two unpaired electrons is correctly antisymmetrised, the correction we obtain is only $O(1/N)$.

(HOLE) BIPOLARON: Both (1) and (2) are decreased by $\approx U_{\text{eff}}$, as the result of the excitation is a polaron (ignoring the unpaired electron in the band as usual). (3) is, of course, forbidden for a bipolaron. In the case of an electron bipolaron, the energy changes are the same, with (1) and (2) representing respectively transitions from the higher and lower localised states to the conduction band.

(HOLE) POLARON: (1) and (3) will be unaffected by Coulomb interaction. Transition (2) will create what is essentially an exciton (although with a hole added to the valence band), and thus this transition is predicted to be split according to the spin of the excited electron. Note, however, that we do not expect polarons to be formed on photoexcitation.

(SINGLET) EXCITON: The states resulting from transitions (1) and (2) are

essentially polaronic, with no Coulomb energy, while transition (3) gives a state which is locally charge neutral and has no unpaired electrons, and which therefore has no Coulomb energy either. We would thus expect all three transitions to be reduced in energy by U_{eff} .

Photoinduced absorption measurements on trans-polyacetylene have shown an absorption peak at 0.48eV (Blanchet *et al.* 1983), which is taken to be absorption due to charged solitons; it has been shown by Ball *et al.* (1983) that charged, rather than neutral, solitons would be expected on photoexcitation. This implies that $U_{\text{eff}} \approx 0.44\text{eV}$ for solitons in t-PA, and that U itself is therefore of the order of 5eV.

In principle, it should be possible to identify defects in conjugated polymers without a degenerate ground state by their absorption patterns. If we disregard Coulomb interactions, the transition energies satisfy two main rules:

$$E(1) + E(2) = E_g \quad \text{and} \quad E(1) + E(3) = E(2)$$

For polarons, these rules are substantially altered by the predicted splitting of transition (2); for bipolarons or excitons, which we expect to be the species formed on photoexcitation, the rules become:

$$E(1) + E(2) = E_g - 2U_{\text{eff}} \quad \text{and} \quad E(1) + E(3) = E(2) - U_{\text{eff}}$$

It will, unfortunately, be difficult to distinguish between (singlet) excitons and bipolarons except by the presence or absence of transition (3).

Photoinduced absorption measurements on polythiophene by Vardeny *et al.* (1986) show two absorptions, at 0.45eV and 1.25eV. The band gap in polythiophene is 2.2eV, from which we calculate a value of $U_{\text{eff}} \approx 0.25\text{eV}$. Note that in the limiting case of no confinement (where a bipolaron essentially consists of two well-separated solitons), U_{eff} for a bipolaron is half that for a soliton. The two values found experimentally are very close to satisfying this relation, which is consistent with there being only weak confinement (i.e. weak ground state non-degeneracy) in

polythiophene (Vardeny finds $\gamma=0.27$, compared with the estimated value for cis-polyacetylene of $\gamma\approx 0.7$).

Vardeny *et al.* claim that their data prove that photoinduced absorption in polythiophene is due to bipolarons - in fact, it is not clear that excitons are not the defects responsible, particularly as we would expect excitons to be the species formed initially on photoexcitation. The third absorption predicted if excitons were responsible would occur at 0.55eV, and the high-energy tail of the observed 0.45eV peak is sufficiently broad to obscure this (in fact, there does appear to be a slight "hump" in the spectrum obtained by Vardeny *et al.* at about this value, but this observation should be treated with extreme caution).

Although the Hubbard U appears able to account for the positions of the photoinduced absorption peaks in both t-PA and polythiophene, the question of the relative absorption weights of the three peaks remains unresolved: the ratio between the absorption intensities of transitions (1) and (2) is observed to be ≈ 1.5 , while the SSH model predicts a ratio of between 10 and 20 for this level of confinement, also predicting that, if excitons rather than bipolarons are the species responsible, transition (3) should have similar weight to transition (1). This is a problem that can only be overcome if CCS can be discarded; in §6.10 the results obtained by using a method which does not display CCS are presented, and are seen to be in good agreement with experiment.

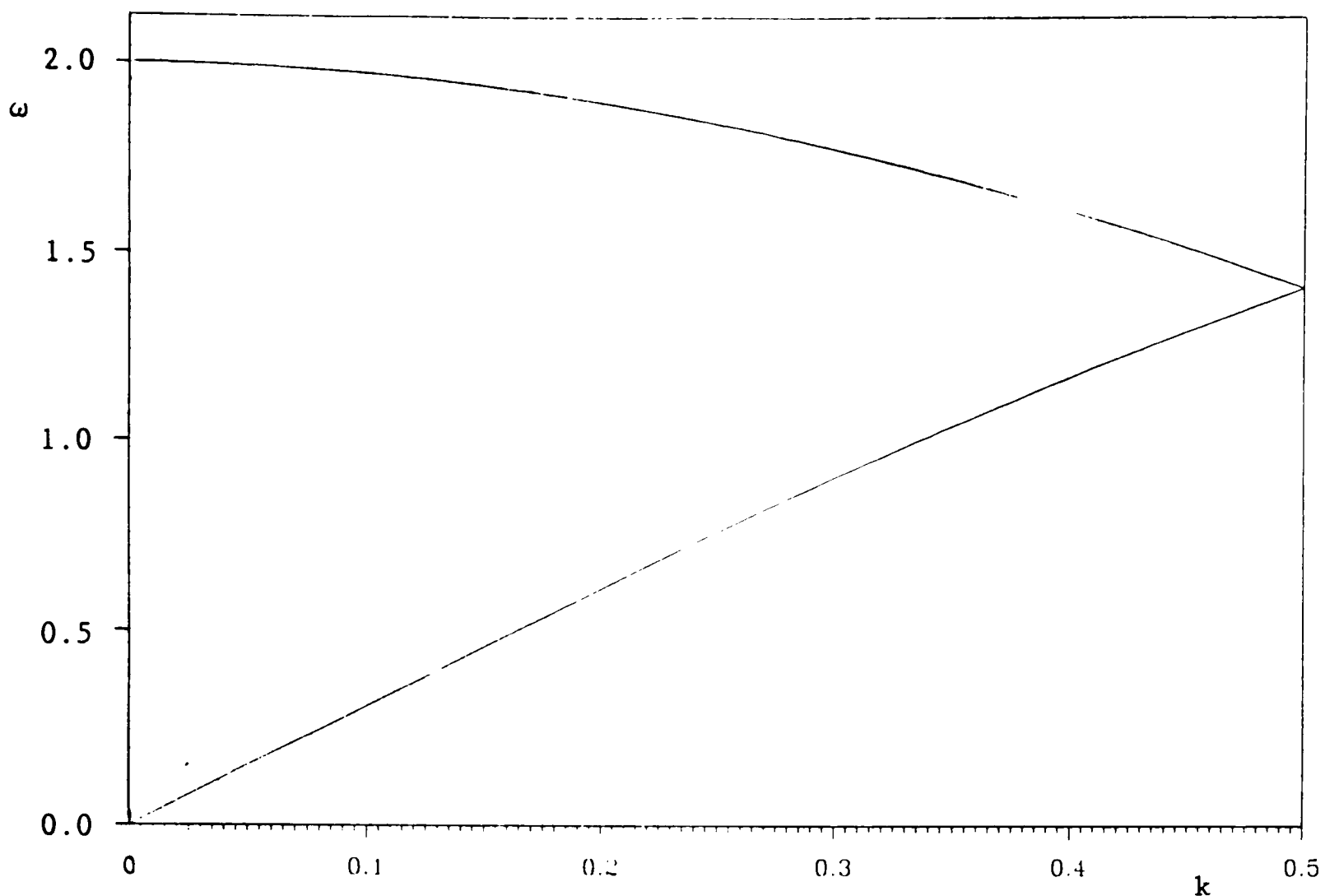


Fig. 3.1 Dispersion relation for undimerised t-PA, ignoring electron-phonon coupling (in figs. 3.1 to 3.3, the frequencies are plotted in units of $\sqrt{K/M}$, which is approximately 950cm^{-1} , and the wave vectors in units of π/a). Here the theoretical result that $\omega = 2\sqrt{K/M} \cdot \sin(ka/2)$ is obtained by putting $\Lambda=0$ in (3.2) (p. 3.6).

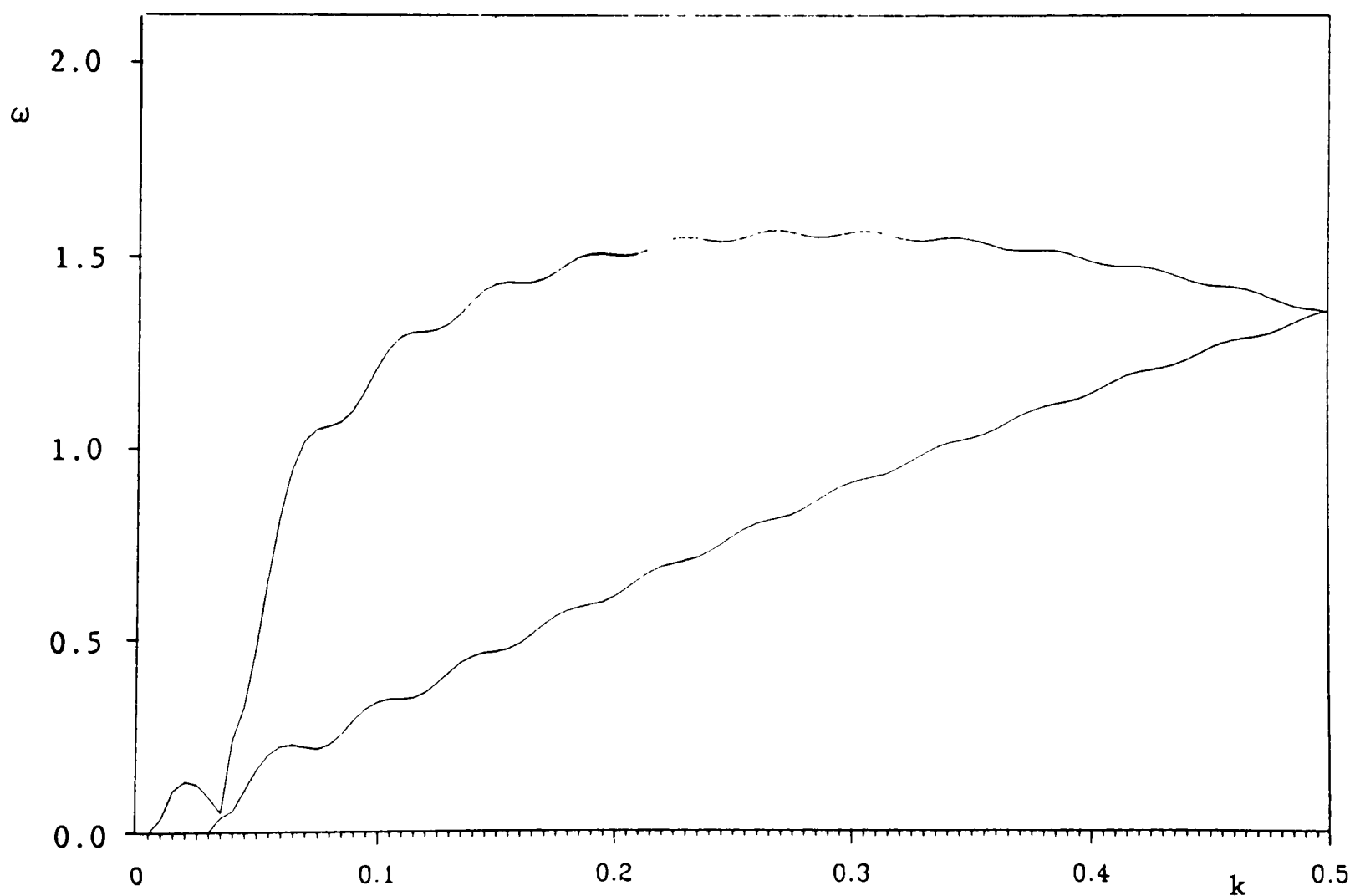


Fig. 3.2 Dispersion relation for undimerised t-PA, including the effect of electron-phonon coupling; this curve was obtained by using the SSH value $\Lambda=0.21$ in (3.2). The oscillations in ω show that long-range effects are significant and the soft mode at $k=0$ in the LO band is easily seen.

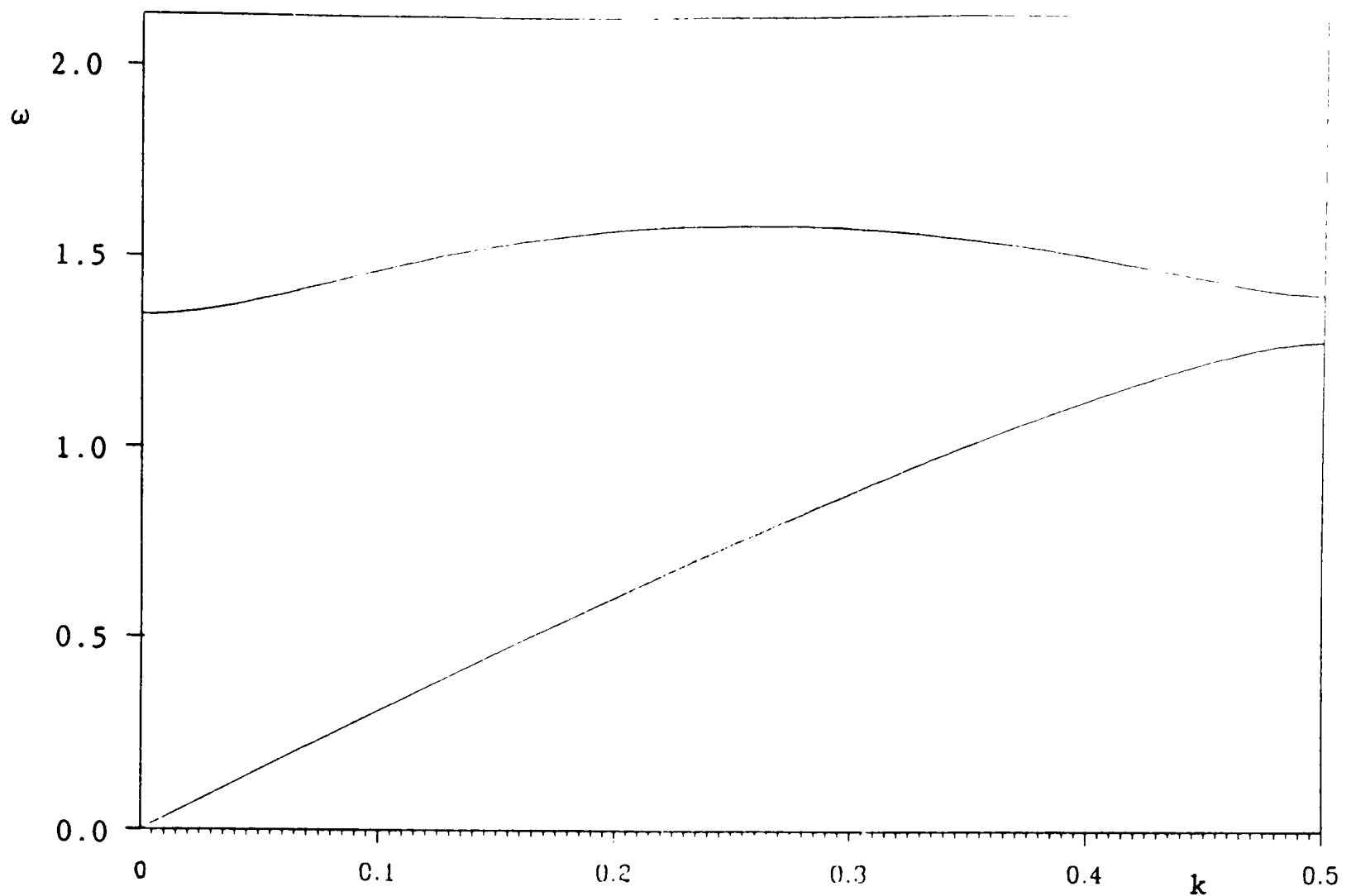


Fig. 3.3 Dispersion relation for dimerised t-PA, including electron-phonon coupling (the integrals in (3.4) (p. 3.8) were calculated with the dimensionless dimerisation parameter z taking its observed value of 0.14). Note the reduction in frequency of the $k=0$ LO phonon from its uncoupled value, and the flatness of the optic band.

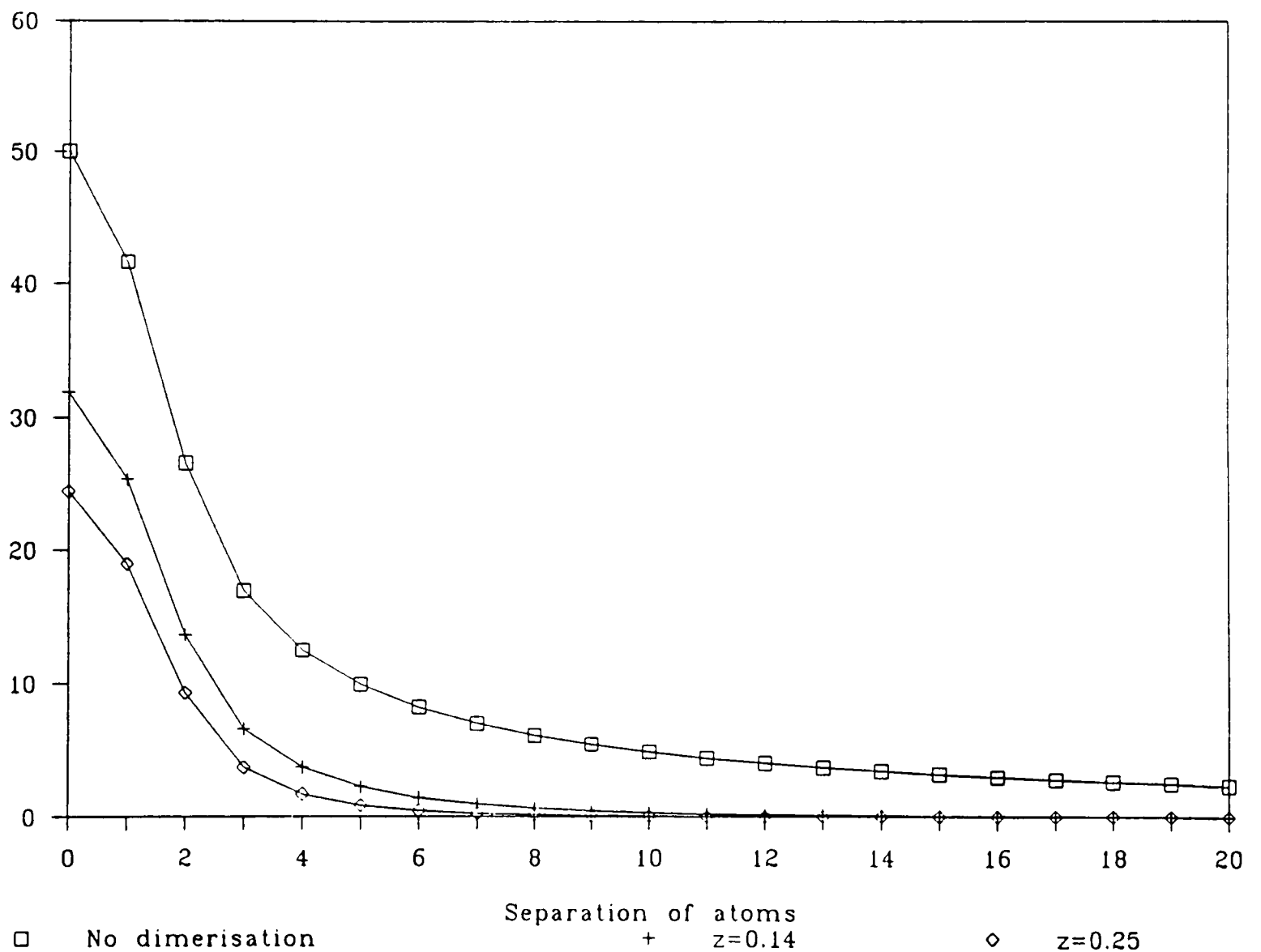


Fig. 3.4 Graph showing how $V_1(n)$, the effective coupling strength between n 'th nearest neighbour atoms (see (3.3), p. 3.7 - plotted in arbitrary units) decays with distance, the decay rate being drastically increased by dimerisation. The central curve ($z=0.14$) corresponds to the observed value.

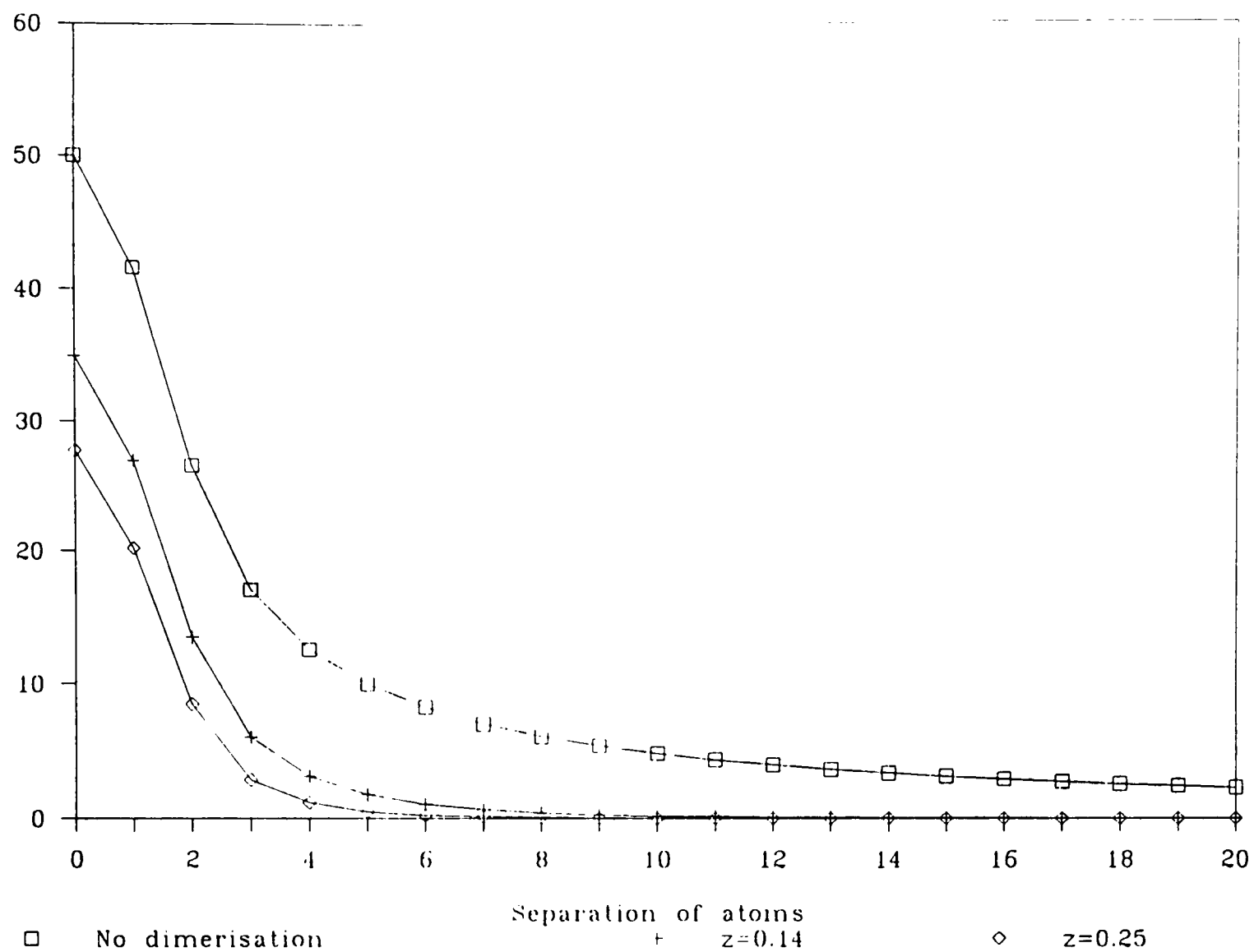


Fig. 3.5 As fig. 3.4, but plotting $V_1(n) + (-1)^n V_2(n)$ instead of $V_1(n)$ alone (see text). The effect is a slight further increase in the speed at which coupling decreases with distance.

4.1 INTRODUCTION

The SSH model Hamiltonian has four principal shortcomings:

- (i) Failure to deal with electron-electron interaction in any form. Even adding a Hubbard U to represent this interaction fails to solve some of the problems associated with charge conjugation symmetry, such as the anomalous absorption strengths of the individual peaks in a polaronic defect (see §§2.5 and 3.7).
- (ii) Inflexibility. The SSH model was designed for use with t-PA, and its application to other polymers raises three distinct problems: the treatment of polymers without two degenerate ground states (we shall see in chapter 6 that the arbitrary methods normally used lead to an underestimation of the distortion at a defect), the effects of atoms other than carbon (the electronegativity of nitrogen, for example, might significantly affect the properties of polypyrrole) and the modelling of polydiacetylenes, where the effective unit cell contains four carbon atoms rather than two.
- (iii) One-dimensionality. Not only does the SSH model preclude the possibility of treating any transverse phonon modes, but the distortion of a chain caused by a dopant ion, for example, is also limited to the axis of the chain. As will be seen in §6.5, significant distortion perpendicular to the plane of the chain is also predicted.
- (iv) Consideration of carbon-carbon interactions only. Since only the carbon p_z orbitals are considered in the SSH model, the possibility of charge storage on the attached hydrogen atoms is ignored (and it will be shown in §6.3 that this is a significant effect when considering how the charge associated with a defect is distributed). Furthermore, the only means of modelling a dopant-induced defect is as a charge added to the chain, perhaps associated with some form of potential to represent

the dopant counterion (see e.g. Bryant and Glick 1982). In reality, the charge transfer may not be complete, and any guess of the dopant-induced potential must be fairly arbitrary. The case of an Li-doped chain of t-PA will be considered, within the framework of the method outlined in this chapter, in section 6.5.

There do exist standard quantum chemical methods for calculating molecular wave functions, within an LCAO basis, given a molecular geometry; these are based on semi-empirical application of Hartree-Fock theory, and are discussed briefly in §§4.2-4.4 (and in more detail by Pople and Beveridge 1970, and Sadlej 1975). They are in the most part, however, designed to be used in cases where the molecular geometry is known or can be assumed, and are not ideally suited to the calculation of a minimum-energy geometry as well as the wave functions. Early calculations of ground state geometries using these methods, for example, worked entirely by trial and error (Pople and Beveridge 1970, chapter 4). Although some more modern programs, such as MOSES (Harker and Lyon 1979), have been modified to perform some degree of geometry optimisation, the methods they use tend to involve either discrete stepping or some extent of numerical differentiation, both of which are fairly time-consuming methods.

The method outlined below relaxes a molecule by a molecular dynamical method, and thus requires no second derivatives to be calculated; the first derivatives required are calculated analytically, by methods outlined in §§4.5 and 4.6, rather than numerically. The wave function calculation (which involves the recursive diagonalisation of an $N \times N$ matrix, where N is the number of basis orbitals used) is the time-limiting step of the calculation, except for very small systems, and is performed in parallel with the molecular geometry calculation, so that just one step of the recursion is performed at each molecular geometry encountered along the minimisation path. This concept of simultaneous geometry optimisation and wave function calculation is due to Car and Parrinello (1985), although the

actual method of wave function calculation they suggested is unsuitable in this case, for reasons discussed in §§4.7 and 4.8.

There are two further advantages to this method of geometry optimisation. Since the method has a dynamical basis, it can be used to obtain good approximate dynamics for a system, simply by not damping out the atomic motion; in particular, there is no need to calculate any second derivatives (which is an intractable process analytically; the calculation of analytic first derivatives is only made possible by the Hellman-Feynman theorem, which enables us to ignore the derivatives of the bond order matrix). It should be noted, though, that the semi-empirical methods used here (INDO, and in particular CNDO) tend to over-predict force constants by a factor of approximately 2-3, so that calculated frequencies will tend to be too high by something like 50-70% (fortunately, this over-prediction is so regular as to be almost systematic (Sadlej 1975, table 5.4), and can be compensated for to some extent).

The second advantage inherent in this method of molecular relaxation is its flexibility (and the computer program used has been written with this in mind); external fields (both electric and force fields) can be applied (and they need not be uniform), and individual atoms may be constrained to remain fixed with respect to motion along any axis. These extensions are discussed further in §4.9.

4.2 HARTREE-FOCK THEORY AND THE ZDO APPROXIMATION

The two basic approximations of Hartree-Fock theory are the Born-Oppenheimer approximation and the assumption that the overall wave function can be written in terms of a Slater determinant of one-electron wave functions. These one-electron functions are made up of a linear combination of atomic orbitals, in general either Gaussian orbitals of some form or Slater-type orbitals (STO's). The latter basis is used here, and will be discussed further below. It can be assumed, without loss of

generality, that both the basis orbitals and the expansion coefficients are real.

By expressing the wave functions in LCAO terms as:

$$\psi_i^\alpha = \sum_{\nu} c_{\nu i}^\alpha \varphi_{\nu} \quad \psi_i^\beta = \sum_{\nu} c_{\nu i}^\beta \varphi_{\nu}$$

where α and β are used to distinguish between the different spin states, the Schrodinger equation is replaced by a pair of matrix equations, where the elements of the matrices are the molecular orbital expansion coefficients. Standard practice is to label atomic orbitals with Greek suffices and molecular orbitals with Roman. These matrix equations (the Hartree-Fock-Roothaan, or HFR, equations) are:

$$\sum_{\nu} (F_{\mu\nu}^\alpha - \lambda_1^\alpha S_{\mu\nu}) c_{\nu i}^\alpha = 0 \quad \text{or} \quad F^\alpha \cdot c^\alpha = S \cdot c^\alpha \cdot \lambda^\alpha$$

and similarly for β . Here λ^α and λ^β are the (diagonal) matrices of one-electron energies, S is the overlap matrix, defined in the obvious way, and F^α and F^β are the Fock matrices, which are derived by adding corrections to the one-electron part of the Hamiltonian to represent electron-electron interaction, and are defined by:

$$F_{\mu\nu}^\alpha = H_{\mu\nu} + \sum_{\lambda\sigma} [P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^\alpha(\mu\sigma|\lambda\nu)]$$

$$F_{\mu\nu}^\beta = H_{\mu\nu} + \sum_{\lambda\sigma} [P_{\lambda\sigma}(\mu\nu|\lambda\sigma) - P_{\lambda\sigma}^\beta(\mu\sigma|\lambda\nu)]$$

where H is the one-electron Hamiltonian matrix and P^α and P^β are the bond order matrices, defined in turn by:

$$P_{\lambda\sigma}^\alpha = \sum_i^{\text{occ}} c_{\lambda i}^\alpha c_{\sigma i}^\alpha \quad P_{\lambda\sigma}^\beta = \sum_i^{\text{occ}} c_{\lambda i}^\beta c_{\sigma i}^\beta \quad P_{\lambda\sigma} = P_{\lambda\sigma}^\alpha + P_{\lambda\sigma}^\beta$$

$$\text{and } (\mu\nu|\lambda\sigma) \equiv \int d\mathbf{r}_1 \int d\mathbf{r}_2 \varphi_\mu(1) \varphi_\nu(1) |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \varphi_\lambda(2) \varphi_\sigma(2)$$

The units used throughout this chapter are atomic units, in which $4\pi\epsilon_0=1$.

The total electronic energy in Hartree-Fock theory is given by:

$$E_{el} = \frac{1}{2} \sum_{\mu\nu} \{ P_{\mu\nu}^\alpha (H_{\mu\nu} + F_{\mu\nu}^\alpha) + P_{\mu\nu}^\beta (H_{\mu\nu} + F_{\mu\nu}^\beta) \}$$

and it is clear that, in principle, a large number of two-electron integrals will have to be calculated before we obtain the Fock matrix or

the electronic energy.

The Zero Differential Overlap (ZDO) approximation (Parr 1952) has two parts, and consists of the neglect of a large number of these integrals. The first part of the approximation consists of assuming orthogonality between basis functions, i.e. replacing $S_{\mu\nu}$ by $S_{\mu\mu}\delta_{\mu\nu}$ above. The second part is the assumption:

$$(\mu\nu|\lambda\sigma) = (\mu\mu|\lambda\lambda)\delta_{\mu\nu}\delta_{\lambda\sigma}$$

It is important to note a couple of points: although the assumption that the wave functions are orthogonal may actually be a very poor reflection of the truth, the error may not be damaging, since it can be shown (Löwdin 1950) that there exists a different set of basis functions (known, for obvious reasons, as Orthogonalised Atomic Orbitals), into which the STO's can easily be transformed in such a manner that the off-diagonal overlaps are zero and the diagonal overlaps are very similar to those of the STO's. A somewhat more rigorous exposition of this argument is given by Sadlej (1975, pp.73ff.).

The second point to note concerns the consistency of these approximations: if an integral is assumed to be zero when expressed in terms of one set of basis functions, it should remain zero when expressed in terms of a different basis. Examples of a change of basis are a rotation of local co-ordinate axes (thus mixing the p-orbitals) or hybridisation (which will mix s and p-orbitals of the same principal quantum number). This invariance is discussed more fully by Pople and Beveridge (1970) and manifests itself, among other ways, by requiring that the Coulomb integral $(\mu\mu|\lambda\lambda)$ be independent of the angular dependence of the basis functions; it is therefore a consequence of the ZDO approximation that we can express all Coulomb integrals in terms of s-orbitals and they will be functions of interatomic distance only.

4.3 SEMI-EMPIRICAL METHODS

In order properly to study the nature of defects in conjugated polymers, we clearly need to work on molecules much longer than a typical defect. Although the half width of a defect is less than 10 carbon units, we really need to work with chains at least 25 carbon units long in order to avoid any appreciable distortion of the defect due to the chain ends; hence the smallest suitable molecule is something like $C_{25}H_{27}$. For molecules of this size, it is clearly out of the question to attempt any kind of *ab initio* calculation of the wave functions and we must implement some of the standard semi-empirical methods available. Those used here are CNDO/2 (the original CNDO method is now no longer used, and the qualification '/2' will henceforth be dropped) and INDO. CNDO (Complete Neglect of Differential Overlap) assumes the ZDO approximation completely, while INDO (Intermediate Neglect of Differential Overlap) retains all one-centre, two-electron integrals, assuming ZDO only for two-centre integrals. Because of symmetry considerations, the only extra integrals that INDO retains are one-centre exchange integrals of the form $(\mu\nu|\mu\nu)$. Further approximations of the two methods are involved in calculating the Hamiltonian matrix elements, and are outlined by Pople and Beveridge (1970). CNDO and INDO calculate two-centre terms in the same manner, and so the two-centre components of the Fock matrices will differ only in that the bond order matrices will not be the same.

The open-shell matrix elements in INDO are:

$$F_{\mu\mu}^{\alpha} = U_{\mu\mu} + \sum_{\lambda \rightarrow A} [P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - P_{\lambda\lambda}^{\alpha}(\mu\lambda|\mu\lambda)] + \sum_{B \neq A} (P_{BB} - Z_B)\gamma_{AB}$$

$$F_{\mu\nu}^{\alpha} = (2P_{\mu\nu} - P_{\mu\nu}^{\alpha})(\mu\nu|\mu\nu) - P_{\mu\nu}^{\alpha}(\mu\mu|\nu\nu) \quad (\mu, \nu \text{ on same atom})$$

$$F_{\mu\nu}^{\alpha} = \frac{1}{2}K_{AB}S_{\mu\nu}(\beta_A^0 + \beta_B^0) - P_{\mu\nu}^{\alpha}\gamma_{AB} \quad (\mu \text{ on A, } \nu \text{ on B})$$

where $P_{AA} = \sum_{\mu \rightarrow A} P_{\mu\mu}$ and Z_B is the charge on the core of atom B.

The terms in these matrix elements fall into three categories:

(i) $\{U_{\mu\mu}\}$, $\{\beta_A^0\}$ and the one-centre, two-electron integrals are

constant parameters of the method and can be set at the start of the calculation. The integrals have been calculated *ab initio* and are tabulated, while standard values, optimised for a broad range of compounds, exist for the other parameters (Pople & Beveridge 1970); note that no parameters are chosen explicitly to optimise the results of calculations on conjugated polymers. K_{AB} is chosen (entirely empirically) to be unity, unless either atom A or atom B is from the third row of the periodic table, in which case $K=0.75$.

(ii) $\{P_{\mu\nu}\}$ etc. need to be recalculated whenever we update our estimate of the wave function.

(iii) $\{S_{\mu\nu}\}$ and $\{\gamma_{AB}\}$ also need to be recalculated periodically, but in this case they depend on the estimated atomic geometry, rather than directly on the wave functions.

The total energy in INDO is given by the rather unwieldy expression:

$$\begin{aligned}
 E = & \sum_{\mu} P_{\mu\mu} (U_{\mu\mu} - \sum_{B \neq A} Z_B \gamma_{AB}) + \frac{1}{2} \sum_{\mu} \sum_{\lambda \rightarrow A} (P_{\mu\mu} P_{\lambda\lambda} - (P_{\mu\lambda}^{\alpha})^2 - (P_{\mu\lambda}^{\beta})^2) (\mu\mu | \lambda\lambda) \\
 & + \frac{1}{2} \sum_{\mu} \sum_{\lambda \rightarrow B} (P_{\mu\mu} P_{\lambda\lambda} - (P_{\mu\lambda}^{\alpha})^2 - (P_{\mu\lambda}^{\beta})^2) \gamma_{AB} \\
 & + \frac{1}{2} \sum_{\mu} \sum_{\nu \rightarrow A} (\mu\nu | \mu\nu) (2P_{\mu\nu}^2 - P_{\mu\mu}^{\alpha} P_{\nu\nu}^{\alpha} - P_{\mu\mu}^{\beta} P_{\nu\nu}^{\beta} - (P_{\mu\nu}^{\alpha})^2 - (P_{\mu\nu}^{\beta})^2) \\
 & + \frac{1}{2} \sum_{\mu} \sum_{\nu \rightarrow B} K_{AB} S_{\mu\nu} (\beta_A^0 + \beta_B^0) P_{\mu\nu} + \sum_A \sum_{B < A} Z_A Z_B R_{AB}^{-1}
 \end{aligned}$$

In this expression, orbital μ is attached to atom A and it is understood that a summation over two orbitals or atoms explicitly excludes the case where they are the same.

This expression does not simplify a great deal, but, subject to one important assumption, the derivative of the total energy with respect to a general atomic co-ordinate X_i is somewhat more simple, since only $\{S_{\mu\nu}\}$ and $\{\gamma_{AB}\}$ of the electronic parameters actually involve two-centre integrals:

$$\begin{aligned}
 \frac{\partial E}{\partial X_i} = & - \sum_{\mu} \sum_{B \neq A} P_{\mu\mu} Z_B \frac{\partial \gamma_{AB}}{\partial X_i} + \frac{1}{2} \sum_{\mu} \sum_{\lambda \rightarrow B} (P_{\mu\mu} P_{\lambda\lambda} - (P_{\mu\lambda}^{\alpha})^2 - (P_{\mu\lambda}^{\beta})^2) \frac{\partial \gamma_{AB}}{\partial X_i} \\
 & + \frac{1}{2} \sum_{\mu} \sum_{\nu \rightarrow B} (\beta_A^0 + \beta_B^0) K_{AB} \frac{\partial S_{\mu\nu}}{\partial X_i} P_{\mu\nu} - \sum_A \sum_{B < A} Z_A Z_B R_{AB}^{-2} \frac{\partial R_{AB}}{\partial X_i}
 \end{aligned}$$

$$\begin{aligned}
= & - \frac{1}{2} \sum_{\mu} \sum_{\lambda \rightarrow B} ((P_{\mu\lambda}^{\alpha})^2 + (P_{\mu\lambda}^{\beta})^2) \frac{\partial \gamma_{AB}}{\partial X_i} + \frac{1}{2} \sum_{\mu} \sum_{\nu \rightarrow B} (\beta_A^0 + \beta_B^0) K_{AB} \frac{\partial S_{\mu\nu}}{\partial X_i} P_{\mu\nu} \\
& - \sum_A \sum_{B < A} (Z_A Z_B R_{AB}^{-2} \frac{\partial R_{AB}}{\partial X_i} - P_{AA} P_{BB} \frac{\partial \gamma_{AB}}{\partial X_i}) - \sum_{A \neq B} \sum P_{AA} Z_B \frac{\partial \gamma_{AB}}{\partial X_i}
\end{aligned}$$

This last form makes the physical meaning of each term clear: the first term represents the force due to the exchange interaction between electrons on atoms A and B; the second represents the electronic overlap, the third the electron-electron and core-core repulsion, and the fourth the attraction between electrons on atom A and the core of atom B. Exactly the same expression applies for CNDO, of course.

The assumption we have made is that we can neglect the derivatives of the bond order matrices P^{α} and P^{β} in calculating the energy derivatives. If we were using the full, many-electron Hamiltonian, and if our approximate eigenfunctions $\{\psi_i\}$ were exact, this would be justified by the Hellman-Feynman theorem. As it is, it has been shown by Slater (1974, Appendix 2) that this assumption is also valid in Hartree-Fock theory, provided that the eigenfunctions are exact (Slater's proof is outlined in the case of X- α theory, but relies only on the wave functions being calculated by a variational principle for its validity, so applies in Hartree-Fock theory too). Since our estimated eigenfunctions are expected to remain very close to the exact (Born-Oppenheimer) solutions, we do not expect this approximation to introduce serious errors. Empirically, it has been shown that energy minimisation calculations where the atoms are moved according to the calculated forces do indeed result in a monotonically reducing energy down to better than 10^{-6} eV, so any errors in the calculated forces must be very small indeed.

The force acting on an atom is given by $F = -\nabla E$, so, using M_i for the mass of atom i and X_i as an atomic co-ordinate:

$$M_i \ddot{X}_i = - \frac{\partial E}{\partial X_i}$$

On using the Verlet algorithm (1967) to expand the atomic co-ordinates as a second order Taylor series, using a time step h and damping by a factor

ξ (i.e. reducing all atomic velocities by a factor ξ at each step), we obtain:

$$X_i(t+h) = -\frac{h^2}{M_i} \frac{\partial E}{\partial X_i} + (1+\xi)X_i(t) - \xi X_i(t-h)$$

Efficient choice of h and ξ is fairly important if we are to reach a minimum energy geometry as quickly as possible; a guide to how this may be done is given as Appendix 1.3.

We are now (in principle) able to perform the simulated annealing process and minimise the energy of the system. All that remains is to calculate the overlap and Coulomb integrals $S_{\mu\nu}$, γ_{AB} and their derivatives with respect to atomic co-ordinates. Clearly, this is at the heart of this method, and the methods used are outlined below, after a brief description of the STO's we use as a basis set.

4.4 SLATER TYPE ORBITALS - BASIS FUNCTIONS

Slater type orbitals are defined in terms of three quantum numbers and an orbital exponent by:

$$\varphi(n,l,m,\zeta) = N(n)Y_{lm}r^{n-1}e^{-\zeta r}$$

The orbital exponent ζ is related to the three quantum numbers according to various sets of (empirically derived) rules (in particular, in CNDO and INDO ζ is treated as a function of n only); if the rules of Slater (1930) are used (as they are here) it is correct to label the orbitals as Slater orbitals, but a number of the orbitals we generate on differentiation do not obey these rules and, to avoid mixing the two terms, the label STO will continue to be used throughout this work.

The radial normalisation factor $N(n)$ is easily calculated to be:

$$N(n) = \left[\frac{(2\zeta)^{2n+1}}{(2n)!} \right]^{\frac{1}{2}}$$

so $N(1) = (4\zeta^3)^{\frac{1}{2}}$ and $N(2) = (4\zeta^5/3)^{\frac{1}{2}} = N(1).(\zeta/\sqrt{3})$, and the properly normalised angular parts $\{Y_{lm}\}$ are given by:

$$Y_{00} = \sqrt{1/4\pi}$$

$$\begin{aligned}
Y_{10} &= \cos\theta \cdot \sqrt{3/4\pi} \\
Y_{11} &= e^{i\varphi}\sin\theta \cdot \sqrt{3/8\pi} & Y_{1,-1} &= e^{-i\varphi}\sin\theta \cdot \sqrt{3/8\pi} \\
Y_{20} &= (3\cos^2\theta - 1) \cdot \sqrt{5/16\pi} \\
Y_{21} &= e^{i\varphi}\sin\theta\cos\theta \cdot \sqrt{15/8\pi} & Y_{2,-1} &= e^{-i\varphi}\sin\theta\cos\theta \cdot \sqrt{15/8\pi} \\
Y_{22} &= e^{2i\varphi}\sin^2\theta \cdot \sqrt{15/32\pi} & Y_{2,-2} &= e^{-2i\varphi}\sin^2\theta \cdot \sqrt{15/32\pi}
\end{aligned}$$

The orbitals that we use for our calculations are not STO's as originally defined, however, but real combinations of STO's with angular parts chosen such that the orbitals "point" along clearly defined directions. The reason for this is that the integration routines rely on the line joining atoms to be the z axis. Since it will in general be necessary to rotate the local co-ordinate system for this to be the case, it is clearly an advantage to work with wave functions which transform in as simple a manner as possible under this rotation. Note that we are free to mix states of the same $|m|$ (in orthogonal combinations), since the overlap integrals depend only on $|m|$, and not on the sign of m itself.

The real combinations we use are defined by:

$$\begin{aligned}
p_x &= -(Y_{11} - Y_{1,-1})/\sqrt{2} &= \sin\theta\cos\varphi \cdot \sqrt{3/4\pi} \\
p_y &= i(Y_{11} + Y_{1,-1})/\sqrt{2} &= \sin\theta\sin\varphi \cdot \sqrt{3/4\pi} \\
p_z &= Y_{10} &= \cos\theta \cdot \sqrt{3/4\pi} \\
d_{z^2} &= Y_{20} &= (3\cos^2\theta - 1) \cdot \sqrt{5/16\pi} \\
d_{xz} &= -(Y_{21} - Y_{2,-1})/\sqrt{2} &= \sin\theta\cos\theta\cos\varphi \cdot \sqrt{15/4\pi} \\
d_{yz} &= i(Y_{21} + Y_{2,-1})/\sqrt{2} &= \sin\theta\cos\theta\sin\varphi \cdot \sqrt{15/4\pi} \\
d_{xy} &= -i(Y_{22} - Y_{2,-2})/\sqrt{2} &= \sin^2\theta\sin 2\varphi \cdot \sqrt{15/16\pi} \\
d_{x^2-y^2} &= (Y_{22} + Y_{2,-2})/\sqrt{2} &= \sin^2\theta\cos 2\varphi \cdot \sqrt{15/16\pi}
\end{aligned}$$

4.5 EVALUATION OF DERIVATIVES FOR ATOMIC RELAXATION

As stated above, the derivatives we need to calculate are those of the Coulomb and overlap integrals:

$$S_{\mu\nu} = \int \varphi_{\mu}(r-R_1)\varphi_{\nu}(r-R_2) dr$$

$$\gamma_{AB} = \iint \varphi_{\mu}^2(r_1-R_1) \cdot \frac{1}{|r_1-r_2|} \cdot \varphi_{\nu}^2(r_2-R_2) dr_1 dr_2$$

with respect to the atomic co-ordinates R_i . The derivatives of the Coulomb integrals are easily obtained from analytic forms derived in Appendix 1.1 and reproduced below; those of the overlap integrals are calculated by differentiating the wave functions, expressing these derivatives in terms of new Slater type orbitals and integrating over these in the usual way (a method originally proposed by Pulay and Török (1973)).

Thus:

$$\begin{aligned} \frac{\partial S_{\mu\nu}}{\partial X_2} &= - \int \varphi_{\mu}(r-R_1) \frac{\partial \varphi_{\nu}(r-R_2)}{\partial x} dr \\ &= - \sum_{\alpha} d_{\nu\alpha} S_{\nu\alpha} \end{aligned}$$

$$\text{where } \frac{\partial \varphi_{\nu}}{\partial x} = \sum_{\alpha} d_{\nu\alpha} \varphi_{\alpha}$$

The coefficients $\{d_{\nu\alpha}\}$ relating the z-derivatives of one STO to the sum of other STO's were published by Gerratt and Mills (1968) for 1s, 2s and 2p orbitals. They obtained:

φ	$\frac{\partial \varphi}{\partial z}$
1s	$-(\xi/\sqrt{3}) \cdot 1p_0$
2s	$(\xi/3) \cdot 1p_0 - (\xi/\sqrt{3}) \cdot 2p_0$
2p ₀	$\xi \cdot 1s' - (2\xi/\sqrt{15}) \cdot 2d_0 - (\xi/\sqrt{3}) \cdot 2s$
2p _{±1}	$-(\xi/\sqrt{5}) \cdot 2d_{±1}$

where the subscript is the z-component of the angular momentum. The 1p₀ and 1s' orbitals have the same form as would 1p₀ and 1s orbitals, but with the exponent of the n=2 set.

We can obtain expressions for those derivatives not given by Gerratt and Mills in a number of ways. The most elegant involves the use of ladder operators, the most simple consists of writing the wave functions out in Cartesian form and simply differentiating. The results are given below for s and p-orbitals, explicitly in the cases n=1 and n=2, and in general form for n>3 (the general form requires n>1+2):

φ	<u>(i) $\partial\varphi/\partial x$</u>	<u>(ii) $\partial\varphi/\partial y$</u>	<u>(iii) $\partial\varphi/\partial z$</u>
1s	(i) $-(\zeta/\sqrt{3}) \cdot 1p_x$	(ii) $-(\zeta/\sqrt{3}) \cdot 1p_y$	(iii) $-(\zeta/\sqrt{3}) \cdot 1p_z$
2s	(i) $(\zeta/3) \cdot 1p'_x - (\zeta/\sqrt{3}) \cdot 2p_x$	(ii) $(\zeta/3) \cdot 1p'_y - (\zeta/\sqrt{3}) \cdot 2p_y$	(iii) $(\zeta/3) \cdot 1p'_z - (\zeta/\sqrt{3}) \cdot 2p_z$
2p _x	(i) $\zeta \cdot 1s' + (\zeta/\sqrt{15}) \cdot 2d_{z^2} - (\zeta/\sqrt{5}) \cdot 2d_{x^2-y^2} - (\zeta/\sqrt{3}) \cdot 2s$	(ii) $-(\zeta/\sqrt{5}) \cdot 2d_{xy}$	(iii) $-(\zeta/\sqrt{5}) \cdot 2d_{xz}$
2p _y	(i) $-(\zeta/\sqrt{5}) \cdot 2d_{xy}$	(ii) $\zeta \cdot 1s' + (\zeta/\sqrt{15}) \cdot 2d_{z^2} + (\zeta/\sqrt{5}) \cdot 2d_{x^2-y^2} - (\zeta/\sqrt{3}) \cdot 2s$	(iii) $-(\zeta/\sqrt{5}) \cdot 2d_{yz}$
2p _z	(i) $-(\zeta/\sqrt{5}) \cdot 2d_{xz}$	(ii) $-(\zeta/\sqrt{5}) \cdot 2d_{yz}$	(iii) $\zeta \cdot 1s' - (2\zeta/\sqrt{15}) \cdot 2d_{z^2} - (\zeta/\sqrt{3}) \cdot 2s$
ns	(i) $-(\zeta/\sqrt{3}) \cdot [np_x] + \frac{(n-1)}{\sqrt{3}} \cdot \frac{2\zeta}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)p_x]$	(ii) $-(\zeta/\sqrt{3}) \cdot [np_y] + \frac{(n-1)}{\sqrt{3}} \cdot \frac{2\zeta}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)p_y]$	(iii) $-(\zeta/\sqrt{3}) \cdot [np_z] + \frac{(n-1)}{\sqrt{3}} \cdot \frac{2\zeta}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)p_z]$
np _x	(i) $\frac{2\zeta/\sqrt{3}}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)s]$ $- \zeta \{ (1/\sqrt{3}) [ns] - (1/\sqrt{15}) [nd_{z^2}] + (1/\sqrt{5}) [nd_{x^2-y^2}] \}$ $+ \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot \{ (1/\sqrt{3}) [(n-1)s] - (1/\sqrt{15}) [(n-1)d_{z^2}] + (1/\sqrt{5}) [(n-1)d_{x^2-y^2}] \}$	(ii) $-(\zeta/\sqrt{5}) \cdot [nd_{xy}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{xy}]$	(iii) $-(\zeta/\sqrt{5}) \cdot [nd_{xz}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{xz}]$

$$\begin{aligned}
\varphi & \quad \underline{(i) \quad \partial\varphi/\partial x} \quad \underline{(ii) \quad \partial\varphi/\partial y} \quad \underline{(iii) \quad \partial\varphi/\partial z} \\
np_y & \quad (i) \quad -(\zeta/\sqrt{5}) \cdot [nd_{xy}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{xy}] \\
& \quad (ii) \quad \frac{2\zeta/\sqrt{3}}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)s] \\
& \quad - \zeta \{ (1/\sqrt{3})[ns] - (1/\sqrt{15})[nd_{z2}] - (1/\sqrt{5})[nd_{x2-y2}] \} \\
& \quad + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot \{ (1/\sqrt{3})[(n-1)s] - (1/\sqrt{15})[(n-1)d_{z2}] - (1/\sqrt{5})[(n-1)d_{x2-y2}] \} \\
& \quad (iii) \quad -(\zeta/\sqrt{5}) \cdot [nd_{yz}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{yz}] \\
np_z & \quad (i) \quad -(\zeta/\sqrt{5}) \cdot [nd_{xz}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{xz}] \\
& \quad (ii) \quad -(\zeta/\sqrt{5}) \cdot [nd_{yz}] + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)d_{yz}] \\
& \quad (iii) \quad \frac{2\zeta/\sqrt{3}}{[2n(2n-1)]^{\frac{1}{2}}} \cdot [(n-1)s] \\
& \quad - \zeta \{ (1/\sqrt{3})[ns] + (2/\sqrt{15})[nd_{z2}] \} \\
& \quad + \frac{2\zeta(n-2)}{[2n(2n-1)]^{\frac{1}{2}}} \cdot \{ (1/\sqrt{3})[(n-1)s] + (2/\sqrt{15})[(n-1)d_{z2}] \}
\end{aligned}$$

4.6 ANALYTIC FORMS OF THE COULOMB INTEGRALS

As has been mentioned earlier, it is a consequence of the ZDO approximation that all two-centre Coulomb integrals may be taken as functions of the interatomic distance R only, with no angular dependence. The other important variables are the principal quantum numbers of the two atoms concerned (n_a and n_b) and their orbital exponents ζ_a and ζ_b . The integrals are derived in Appendix 1.1, in a form suitable both for implementation in a computer program and for easy differentiation, and they are quoted here.

1. General case: $\zeta_a \neq \zeta_b$

$$\gamma_{AB} = 1/R$$

$$\begin{aligned}
& - e^{-2\zeta_a R} \sum_{m=0}^{2n_a-1} \sum_{p=0}^m \sum_{q=0}^{2n_b-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_b} \frac{(2n_a-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot R^{k+j-1} \\
& \quad \zeta_a^m \zeta_b^{2n_b+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_a - \zeta_b)^{j-2n_b-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_b+m-1-p-q)!}{p!(m-p)!q!(2n_b-1-q)!k!j!} \\
& - e^{-2\zeta_b R} \sum_{m=0}^{2n_b-1} \sum_{p=0}^m \sum_{q=0}^{2n_a-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_a} \frac{(2n_b-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot R^{k+j-1} \\
& \quad \zeta_b^m \zeta_a^{2n_a+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_b - \zeta_a)^{j-2n_a-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_a+m-1-p-q)!}{p!(m-p)!q!(2n_a-1-q)!k!j!}
\end{aligned}$$

where $J_{a,b} = (2n_{a,b} + m - 1 - p - q)$.

2. Special case: $\zeta_a = \zeta_b = \zeta$

$$\gamma_{AB} = 1/R$$

$$\begin{aligned}
& + e^{-2\zeta R} \cdot \frac{1}{4n_a n_b} \sum_{m=0}^{2n_a-1} \sum_{k=0}^m \sum_{j=0}^{2n_b-1} \sum_{p=0}^{k+j} \frac{(2n_a-m)}{2n_b+m-j-k} [(-1)^j - (-1)^{m-k}] \cdot \\
& \quad \frac{(k+j)! \zeta^{2n_b+m+p-k-j}}{k!j!(m-k)!(2n_b-1-j)!p!2^{k+j+1-p}} \cdot R^{2n_b+m+p-k-j-1} \\
& - \frac{e^{-2\zeta R}}{2n_b} \sum_{a=0}^{2n_b-1} (2n_b-a) \frac{(2\zeta)^a R^{a-1}}{a!}
\end{aligned}$$

4.7 WAVE FUNCTION CALCULATION

In the original method of Car and Parrinello, the wave functions are calculated by a simulated molecular dynamical (MD) method. This is much quicker than a matrix diagonalisation method if the number of basis functions is much larger than the number of occupied orbitals, as is the case in density functional theory, using a plane wave basis. If the number of basis functions is N and the number of occupied orbitals M , orthogonalisation requires M^2 conditions of the form:

$$\sum_{\mu} c_{\mu i} c_{\mu j} = \delta_{ij}$$

to be satisfied. Each condition requires $O(N)$ multiplications and additions, so the total number of operations required is $O(M^2N)$. Straightforward matrix diagonalisation requires $O(N^3)$ operations (although some modern routines can take $O(N^2 \log N)$), so there is a substantial advantage in the Car-Parrinello method if $N \gg M$.

If we are using an LCAO method with an STO basis, however, the numbers of basis functions and of occupied orbitals are similar and this advantage of the MD technique is lost. Given that the programming effort involved in diagonalisation is substantially less than that required if the MD method is used, there seems no reason to retain the MD method of wave function calculation. Brief details of the method are given below, however, along with some of the complications encountered, as it might well prove desirable to implement this method if a Gaussian basis set were to be used in the future (a reliable Gaussian basis set requires many more orbitals than an STO set, although the relevant integrals are easier to perform).

4.8 THE CAR-PARRINELLO METHOD AS APPLIED TO MOLECULAR ORBITALS

Car and Parrinello (1985) proposed extending the molecular dynamical (MD) method used to calculate atomic positions so that it could be applied to the wave functions as well. Just as the atomic co-ordinates to be calculated are determined by the conditions:

$$M_i \ddot{X}_i = - \frac{\partial E}{\partial X_i}$$

they suggested that the same principle be extended to calculation of the wave functions $\{\psi_i\}$, by simply replacing the co-ordinate X_i by ψ_i and introducing a fictitious mass m .

The most complicated part of the Car-Parrinello method lies in ensuring that the wave functions remain orthonormal. In essence, what we are doing is applying an external constraint to the system; a similar problem has

been examined by Ryckaert *et.al.* (1977), who considered the dynamics of small hydrocarbon molecules under the constraint of fixed bond lengths. The key point to remember is that the constraints must be kept exactly satisfied throughout the calculation, even though the wave functions will only satisfy the equations of motion to limited accuracy (i.e. to $O(h^2)$ if we use the same process for updating the wave functions as for the atomic positions above). They proposed two methods for ensuring orthogonality: the constraints can be satisfied simultaneously, by a matrix method, or in turn, by allowing the wave functions to "move" freely, and then orthogonalising. A brief outline of both methods is given below.

MATRIX METHOD

We incorporate into the equations of motion a matrix Λ of Lagrange multipliers to ensure orthonormality:

$$m\ddot{\psi}_i = - \frac{\partial E}{\partial \psi_i} + \sum_j \Lambda_{ij} \psi_j$$

In Hartree-Fock theory (replacing Λ by $\lambda = \Lambda^T$, for reasons that will become apparent) this becomes:

$$m\ddot{\psi}_i = -F\psi_i + \sum_j \lambda_{ji} \psi_j$$

Expressing the wave function in terms of LCAO molecular orbitals as above, we derive the matrix equation:

$$mS.\ddot{c} = -F.c + S.c.\lambda$$

where S is the overlap matrix of the atomic orbitals. Note that at equilibrium this reduces to the Hartree-Fock-Roothaan equations; this is the justification for the validity of this method. It is worth noting that, like the HFR equations, this matrix equation is perfectly general within Hartree-Fock theory, and that we do not have to make the assumptions of CNDO etc. until we actually evaluate the overlap and Fock matrices. More specifically, we have not yet assumed orthogonality of the atomic orbitals.

It is helpful to make the following substitutions:

$$c_- \equiv c(t-h) = c.(I-d)$$

$$c_+ \equiv c(t+h)$$

$$F' = c^T.F.c$$

At this stage we do assume orthogonality of the atomic orbitals (i.e. the first part of the ZDO approximation); it is necessary to assume that the overlap matrix S is constant, and clearly this is an unrealistic assumption unless it is assumed to equal the identity matrix throughout. We obtain c_+ in the same manner as we found the new atomic positions earlier (using η as the damping factor for the wave function "motion"):

$$\begin{aligned} c_+ &= (h^2/m)(-F.c + c.\lambda) + c.(I+\eta d) \\ &= c.[(h^2/m)(-F'+\lambda) + (I+\eta d)] \end{aligned}$$

Applying the orthonormality constraint at time $t+h$ gives:

$$\begin{aligned} 0 &= \eta(1+\eta)(m/h^2)^2(d+d^T) + (m/h^2)(-2F'+2\lambda+\eta(-d^T.F'-F'.d+d^T.\lambda+\lambda.d)) \\ &\quad + (F'^2+\lambda^2-\lambda.F'-F'.\lambda) \end{aligned}$$

which we can write as an equation for the unknown matrix λ :

$$\begin{aligned} 2\lambda &= -\eta(1+\eta)(m/h^2)(d+d^T) + 2F' + \eta(d^T.F'+F'.d-d^T.\lambda-\lambda.d) \\ &\quad - (h^2/m)(F'^2+\lambda^2-\lambda.F'-F'.\lambda) \end{aligned}$$

This cannot be solved for λ directly, but bearing in mind that d is small, we can do so iteratively. The convergence should be fairly rapid if we have chosen a small effective step length (h^2/m).

Two points concerning the "velocity" matrix d should be noted: although d itself is $O(h)$, the first term in the equation above is not $O(1/h)$, since d^T+d is $O(h^2)$. This arises from orthonormality at $(t-h)$, as a consequence of which d can be written as $I - e^A$, where A is an antisymmetric matrix. Secondly, it is not necessary to invert c to calculate d : using orthonormality again, we get $d = I - c^T.c_-$.

THE "SHAKE" METHOD

For reasons not immediately apparent, Ryckaert *et.al.* (1977) gave the above

name to the procedure whereby the constrained co-ordinates, in this case the matrix elements $\{c_{\mu i}\}$ are first moved without the constraints to new values $\{c'_{\mu i}\}$, and the constraints are then applied. If we label the k 'th constraint (representing orthogonality between molecular orbitals i and j) by σ_k , we can introduce an effective force which will lead to an adjustment of the co-ordinate matrix given by:

$$\delta c = \sum_k \lambda_k \frac{\partial \sigma_k}{\partial c}$$

Now the "force" acting on component $c_{\mu p}$ due to constraint k is given by:

$$\frac{\partial \sigma_k}{\partial c_{\mu p}} = c_{\mu i} \delta_{pj} + c_{\mu j} \delta_{pi}$$

so we have:

$$\delta c_{\mu i} = \lambda_{ij} c'_{\mu j} \quad \text{and} \quad \delta c_{\mu j} = \lambda_{ij} c'_{\mu i}$$

giving (assuming λ_{ij} is small):

$$\lambda_{ij} \approx \frac{- \sum c'_{\mu i} c'_{\mu j}}{\sum (c'^2_{\mu i} + c'^2_{\mu j})}$$

Just as in the matrix method above, this yields a recursive process; as we satisfy one constraint, we will in general break the others, and so we must continue the process to consistency (in the case $i=j$, the above equations do not hold and it is sufficient merely to normalise the relevant eigenvector).

DRAWBACKS

Neither of the above methods for calculating the wave functions within the Car-Parrinello framework is entirely satisfactory. The basic problem occurs in the orthonormalisation process, and stems from the fact that the constraints do not specify a unique solution for the wave function. Consider the SHAKE method first. First the wave function is allowed to develop according to the unconstrained equations of "motion", and then it is "moved" to a nearby point on the orthonormality surface. Not only is there no *a priori* guarantee that this will be the lowest energy point, but the point reached depends on the order in which the constraints are

applied. Consider, as a simple example, the case of a 2x2 matrix, of the form $I+a$, where a is a matrix of order h (just as the unconstrained $c(t+h)$ will consist of a unitary matrix with a general matrix of this order added).

$$\text{Writing } a = \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix}$$

then we can either orthogonalise the eigenvectors first, and then normalise, or normalise first and then orthogonalise. In the former case, the matrix resulting from the orthonormalisation process is:

$$\exp \begin{bmatrix} 0 & \frac{1}{2}[\beta(1-\alpha)-\gamma(1-\delta)] \\ -\frac{1}{2}[\beta(1-\alpha)-\gamma(1-\delta)] & 0 \end{bmatrix}$$

while in the latter case, we obtain:

$$\exp \begin{bmatrix} 0 & \frac{1}{2}[\beta(1-\delta)-\gamma(1-\alpha)] \\ -\frac{1}{2}[\beta(1-\delta)-\gamma(1-\alpha)] & 0 \end{bmatrix}$$

and even to $O(h^2)$, which is the accuracy to which we are working with the Verlet algorithm, these matrices are not the same.

The problems encountered in the simultaneous satisfaction of all constraints are even more severe, however. Leaving aside the inflexibility of the method (the equation governing λ depends directly on the equation of "motion"), there is a more serious problem. Consider the equation defining $c(t+h)$:

$$c_+ = c. [(h^2/m)(-F'+\lambda) + (I+\eta d)]$$

The constraint that c_+ is unitary is thus an equation in two variables only, d and $(h^2/m)(-F'+\lambda)$; hence we can express $(h^2/m)(-F'+\lambda)$ as some function of d only, say $F(d)$. This leads to a new equation for c_+ :

$$c_+ = c. [I + \eta d + F(d)]$$

In other words, $c(t+h)$ is a function solely of $c(t)$ and (since d is a function of c and c_-) $c(t-h)$, with no dependence at all on the Fock matrix, so the evolution of the wave function with time is entirely given by the initial conditions and is independent of the nature of the system. This

unhappy state of affairs can be demonstrated for the case $d=0$, which would arise if the wave function were started from "rest"; it is easily seen that the wave function will never start "moving" in this case.

The problem here is clearly one of non-uniqueness again; in this case, λ is found as one specific solution of a matrix equation with a large number of solutions. It is not clear how to modify the method in order to obtain the minimum energy solution instead.

The overall calculation process that is implemented here is conceptually very similar to that used for self-consistent solution of the SSH Hamiltonian (§2.2) and can be summarised as follows:

- (i) An initial geometry is used to derive a first-guess Fock matrix. This is very similar to the Hamiltonian matrix and therefore not very accurate, because it takes no account of the wave functions. It is diagonalised to provide a first estimate of the wave functions, and these are used to improve on the original Fock matrix estimate. The repetition of this process to full self-consistency is the method by which CNDO calculations are performed when geometry optimisation is not required, but for a geometry optimising run or a molecular dynamical run the process is repeated a smaller number of times, typically 3-5; this value is chosen as part of the program's input data (see Appendix 2). This ensures that the Fock matrix is fairly accurate before the atoms start moving; it is the Fock matrix that principally dictates the atomic motion, and a wildly inaccurate matrix will clearly lead to unpredictable results and, at best, slow convergence.
- (ii) Having found a good estimate of the Fock matrix at the initial geometry, the atoms are moved according to the equations of motion outlined in §4.3. The new atomic positions are used to update the old Fock matrix; the result is diagonalised just once, and the wave functions thus obtained are then used to derive a Fock matrix which has had both atomic and electronic components updated once. This step is

then repeated until the convergence criteria (which also form part of the input data) are satisfied. The novel part of this method is the fact that only one Fock matrix diagonalisation is necessary at each geometry encountered on the way to minimisation; previous geometry optimisation routines using CNDO have calculated the Fock matrix to full self-consistency at each geometry. Because of the molecular dynamical nature of the optimisation process used here, however, the system moves only slowly when it is close to the self-consistent geometry, so that the Fock matrix becomes a better and better approximation to the self-consistent form as the program proceeds.

4.9 EXTENSIONS TO THE RELAXATION ROUTINES

It is a simple process to extend the relaxation method to include consideration of various extra forces and constraints. Those implemented at present, with brief details of how they affect the calculation of the molecular energy and the atomic forces, are summarised below (details of how they are actually used are included in the program documentation in Appendix 2).

EXTERNALLY APPLIED FORCES

It may sometimes be desirable to apply external forces to some of the atoms in a molecule (in order to examine the behaviour of a molecule under pressure, for example, or to prevent an unstable system from breaking apart). This is trivially done, by adding the force directly to that calculated as $-\nabla E$, and by adding a term $-\sum F_i \cdot R_i$ to the total energy (although this is not strictly necessary in order to obtain the minimum energy geometry, and the total energy in this case is a fairly arbitrary figure, it is always helpful to be able to see that the energy calculated is indeed decreasing during a calculation, and by how much).

APPLIED FORCE FIELDS AND CONSTRAINTS

When considering the behaviour of certain molecules (in particular

biological molecules, but the same principle could apply to the study of adsorbed gas molecules), it may be advantageous to study them in conjunction with some sort of substrate (which, in the case of biological molecules, will be a receptor molecule of some kind). It may not be feasible directly to incorporate the substrate molecule into the relaxation calculation (either because its nature is not known, or because it is too large for such a calculation to be worthwhile), so the facility has been added to specify an effective force field to represent the substrate. It is also possible to constrain the relaxation by preventing individual atoms from moving in particular directions; an example of this process is given in §5.6.

ELECTRIC FIELDS

The behaviour of molecules in the presence of an electric field is also easily examined. The field need not be uniform throughout the molecule, but there is the constraint that the field at an atom must not vary significantly over a distance shorter than the relevant orbital exponent. If we are concerned with the field due to a point charge, for example, this condition will be satisfied provided that the distance from any atom to the charge is much greater than the orbital exponent (typical orbital exponents are in the range 1-2a.u., or about 0.5-1.0Å, so this should not normally pose a problem). Should it be necessary to work with fields which do vary significantly over a shorter distance than this, the calculations below will need to be repeated without making the approximation that the potential can be expanded to first order about an atomic nucleus.

This is the only one of these extensions that will directly affect the wave functions; the Hamiltonian must be modified to take account of the added potential, by changing its elements by:

$$\delta H_{\mu\nu} = - \langle \mu | V | \nu \rangle$$

Writing $V(R+r) = V(R) - \epsilon(R) \cdot r$, where R represents the atomic position and r the electronic co-ordinates relative to that, it is easily seen, by

symmetry, that the only changes that need to be considered are diagonal elements of the form $\langle \mu | V(R) | \mu \rangle$ and off-diagonal elements of the form $\langle s | \epsilon_x | p_x \rangle$, where the orbitals are centred on the same atom (this is another consequence of the ZDO approximation). The first of these integrals is trivial, as $V(R)$ is independent of r , while the second is easily calculated to be:

$$\langle s | \epsilon_x | p_x \rangle = (2n+1)\epsilon_x / (2\sqrt{3})$$

The effect of the electric field and the electrical potential on the atomic cores is obvious, with contributions to the force on an atom and the energy contribution of the atom given by $Z\epsilon(R)$ and $ZV(R)$ respectively. While the adjustments to the Hamiltonian will affect the energy of the molecule, we must alter the forces explicitly (we had previously assumed that the Hamiltonian matrix elements were independent of position), and the correct force to add is $-P_{AA}\epsilon(R)$, with P_{AA} defined as in §4.3.

FIXING HYDROGEN ATOMS TO THEIR HOST ATOMS

In a number of cases, it may be disadvantageous for the hydrogen atoms in a molecule to be allowed to move freely; the most obvious case occurs when the geometry optimisation would be accelerated by using a large time step, but this time step would lead to instability in the high-frequency oscillations within the molecule (and these will normally be those oscillations involving hydrogen atoms). Accordingly, the facility to "freeze" hydrogen atoms to their host atoms has been included - if necessary, the positions of the hydrogen atoms can be optimised in a separate calculation. Note that the hydrogen atoms feel no forces if they have been fixed to their hosts, but that they just move in parallel (the calculation moves the host atom alone, then moves the hydrogen atom in parallel, rather than treating the host-hydrogen combination as a rigid pair and adding the forces on both).

4.10 IMPLEMENTATION

The relaxation program has been implemented on an IBM-PC for molecules of up to 26 atoms or 65 orbitals, and on an IBM 3084 mainframe for molecules of up to 100 atoms or 300 orbitals (the low ratio of orbitals required per atom is a consequence of the large proportion of hydrogen atoms in the molecules under consideration, since only a valence basis set is used). The latter version has also been implemented on the CRAY-2 mainframe at Harwell. Documentation to the program is included in this thesis as Appendix 2.

The memory required is rather less than $100N^2$ bytes, where N is the number of basis orbitals, and the mainframe version takes up approximately 7.5M of storage. It is clear that this will not be the factor that determines how large a system we can consider, but that this will be decided by the CPU time required. For large systems, calculation time will increase as N^3 , as the matrix diagonalisation is the time-limiting step, but when considering small systems the calculation of overlap integrals and their derivatives will continue to be an important element and the calculation time will increase less quickly. Since overlap integrals may in general be assumed to be small for interatomic separations of greater than about 5Å (they contain a factor $e^{-2\zeta R}$, where the orbital exponent ζ is greater than 1 a.u. for most of the atoms we consider), the facility to specify a limit of atomic separation, beyond which all overlap integrals will be neglected and all Coulomb integrals replaced by $1/R$, is included, which can lead to considerable savings of time when considering long molecules such as the polymer models investigated in this thesis. That the 5Å limit suggested above is a reasonable approximation can be seen by looking at fig. A1.1, in Appendix 1, which plots two sample Coulomb integrals and has a curve of $1/R$ for comparison.

5.1 INTRODUCTION

This new method for self-consistent geometry optimisation and wave function calculation within the CNDO and INDO approximations need not be restricted to the study of conjugated polymers. Its speed and flexibility mean that it can be used to investigate the ground state properties of any systems which are well treated by CNDO and INDO, which include most organic molecules. Since the cost of optimising the geometry of a molecule has been made comparable to the cost of calculating its wave functions at fixed geometry, it is now feasible to calculate the dipole moments of molecules, for example, in their optimal geometry state (§5.3). Even if this does not reproduce the theoretical results more accurately than equivalent results derived using a standard set of bond lengths and angles, it may enable us better to understand the strengths and weaknesses of the CNDO method.

By applying a uniform electric field to the molecule under consideration, we can find theoretical polarisabilities in a non-perturbative manner, and account for that part of the polarisability due to a molecule's ability to distort in a field. The results of these calculations are given in §5.4, and reproduce well the self-consistent perturbative results in the cases where these are available (although a slight improvement on the perturbative results is noticeable).

The study of molecular vibrations is also possible in a number of cases, and may be useful where a valence force potential model is not suitable. The most important example will be discussed in the next chapter, where the effect of electron-phonon coupling on the Raman-active modes of the polyacetylene isomers is examined. Some simple examples are given in §5.5, though, and demonstrate the consistent overestimation of phonon frequencies by CNDO.

The specific application of this method to the field of biochemistry is

considered in §5.6, where the behaviour of the biologically important molecule serotonin is examined in detail. It will be seen that its optimal geometry is radically dependent on its charge state, for example, and the areas of the molecule that are most affected by charging, photoexcitation and protonation are isolated.

5.2 GEOMETRY OPTIMISATION

CNDO has had much success in predicting ground state geometries for a range of (mostly organic) molecules (Pople and Beveridge 1970, §4.2, Sadlej 1975, §5.4). However, the methods used to do so have often been very time-consuming and unreliable (Pople and Beveridge themselves used a discrete stepping method). The method of Powell (1964) was a substantial improvement, although not specifically designed for this purpose; this was a general method of finding the minimum of a function of any number of variables, requiring only the ability to calculate the function at any point in N -dimensional space. McIver and Komornicki (1971) used a Gaussian basis set and calculated first derivatives analytically, as in the method used here, using a variable metric method to optimise the geometry. The latter authors compared the two methods, using the geometry optimisation of ethene as an example. The starting geometry had a C=C bond length of 1.34Å, C-H bond lengths of 1.10Å and all bond angles were 120°. The convergence criterion was that the change in any atomic co-ordinate must not exceed 0.01Å in any step. The Powell method required 37 calculations of the total energy before the geometry met this criterion, while that of McIver and Komornicki required only 7 such calculations. Each energy calculation requires about 5 matrix diagonalisations (they did not specify the precision to which they required the energy), so the two methods required approximately 185 and 35 matrix diagonalisations respectively. For comparison, the method used here required 11 diagonalisations in order to satisfy the same convergence criterion.

Two examples of results generated by the geometry optimisation process are given here. The series obtained by the increasing fluorination of methane is examined, and the ground state geometry of methanol is obtained. In the latter case, the agreement with experiment is excellent in terms of the general shape of the molecule; in the former, the trends observed experimentally are reproduced well qualitatively, albeit less well quantitatively.

Table 5.1 Calculated and experimental geometries of the fluoromethanes

	Bond lengths (Å):		Bond angles (degrees):	
	C-H	C-F	H-C-H	F-C-F
CH ₄	1.114(1.093)		109.5(109.5)	
CH ₃ F	1.118(1.105)	1.344(1.385)	109.7(109.9)	
CH ₂ F ₂	1.121	1.342(1.36)	110.9	102.0(108.5)
CHF ₃	1.123(1.098)	1.341(1.332)		106.3(108.8)
CF ₄		1.338(1.317)		109.5(109.5)

Values in brackets are experimental results (see Pople and Beveridge 1970, table 4.7, for the original references), obtained by different authors in each case. Experimental values of the C-H bond length and H-C-H angle in CH₂F₂ are not available.

The ground state geometry of methanol has been examined experimentally by Ivash and Dennison (1953), and agrees well with that predicted by CNDO (it is well known that CNDO tends to over-predict the O-H bond length by up to 0.1Å). It is correctly predicted that the staggered form is more stable (Fig. 5.1), and that the methyl group is bent away from the C-O bond by a small angle, labelled α in the figure. The value obtained by Ivash and Dennison is slightly larger than that predicted by CNDO, but did rely for its derivation on the assumption that the methyl group was purely tetrahedral, with a C-H bond length 1.09Å. To reach an optimal geometry to

within the convergence criterion of McIver and Komornicki (see above) required only 12 matrix diagonalisations, the equivalent of just three energy calculations at fixed geometry.

Table 5.2 Ground state geometry of methanol

	CNDO Theory	Experiment
C-H bond length	1.121Å	(1.09Å)*
C-O bond length	1.368Å	1.43Å
O-H bond length	1.033Å	0.94Å
C-O-H bond angle	105.2°	105.9°
H-C-H bond angle	108.3°	(109.5°)*
H-C-O bond angle	108.4°, 111.7°	(109.5°)*
H ₃ -C-O angle α	2.2°	3.2°

* assumed (it is not clear how Ivash and Dennison reconcile their assumption that the methyl group is perfectly tetrahedral with their non-zero value for the angle α).

5.3 CHARGE DISTRIBUTION AND DIPOLE MOMENT CALCULATIONS

Most previous calculations of dipole moments predicted by CNDO have assumed that the bonds and angles within the molecule under consideration take an appropriate *standard* value (Pople and Gordon 1967). The reason for this approximation was simply the cost of geometry optimisation by earlier methods. Using this new method, however, the cost of optimising a molecular geometry is comparable to that of calculating the wave functions assuming a fixed geometry. Although CNDO has had much success at predicting molecular dipole moments (Pople and Beveridge 1970, table 4.18) it is interesting to see if these results can be improved with geometry optimisation, or if the differences between theoretical and experimental dipole moments are due to the CNDO method itself.

It should be noted that the dipole moment associated with a bond actually

varies rather slowly with the bond length; considering an HF molecule over a series of bond lengths shows that the charge stored on each atom is slightly reduced as the bond length increases and that the dipole moment associated with the orbitals forming the bond is reduced more substantially, leaving the overall dipole moment changed by at least an order of magnitude less (proportionately) than the bond length.

Table 5.3 Dipole moment of HF, as a function of bond length

Bond length (Å)	Atomic charge	Dipole moment (D)		
		Atoms	Bond	Total
0.90	0.233	1.008	0.839	1.847
0.95	0.229	1.047	0.808	1.855
1.00	0.226	1.087	0.774	1.861
1.05	0.223	1.126	0.740	1.867
1.10	0.221	1.167	0.705	1.872

The bond angles in a molecule may affect the predicted dipole moment, however, and the standard geometrical models fail to account for any change in these from their perfect (tetrahedral, trigonal or linear) values. One obvious case to consider is the series $\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3$, where steric effects are observed (and predicted) to open out the bond angle at the oxygen with increasing size of the attached groups. CNDO correctly predicts that the dipole moment should decrease along this series, but underestimates the extent of this decrease and slightly overestimates the dipole moments themselves. Using optimised geometries rather than the standard geometries does improve the results slightly (because of this increase in the bond angle), but this correction is not sufficient to account for the discrepancy and it is necessary to conclude that the error is inherent in the method.

Table 5.4 Predicted and experimental dipole moments (debyes)

	Standard geometry	Optimised geometry	Experiment ⁽¹⁾
H ₂ O	2.10	2.10	1.85
CH ₃ OH	1.94	1.85	1.69
CH ₃ OCH ₃	1.83	1.75	1.30

(1) see Pople and Beveridge (1970, table 4.18) for the original references.

Another series of molecules worth considering in this context is the fluoromethanes (which were considered above in terms of their geometries). The dipole moments of fluoromethane (CH₃F) and fluoroform (CHF₃) are predicted, using the standard geometries, to be very similar, as should be the case if each fluorine atom attracts an equal charge away from the central carbon atom, irrespective of how many other fluorine atoms are already attached to it. Experimentally, the dipole moment of CH₃F is rather higher (1.855D compared to 1.645D), presumably because the fluorine atoms find it more difficult to attract charge when there are more of them. Using the optimised geometries, however, predicts the reverse (dipole moments of 1.60D and 1.98D for CH₃F and CHF₃ respectively), and it is clear that this is due to the underprediction of the F-C-F bond angle in CHF₃ (table 5.1). It is probably wisest to conclude that while CNDO does predict dipole moments with a fair degree of accuracy, it is not advisable to rely on its predictions when considering small differences between the dipole moments of different molecules, even when the fully optimised geometries are used.

5.4 MOLECULAR POLARISABILITIES

Calculations of molecular polarisabilities have previously been carried out within the CNDO approximation by a perturbative method, assuming fixed molecular geometry (Davies 1969). As with the study of dipole moments (§5.3) it is interesting to see how the use of optimised molecular

geometries affects the results obtained. The method used here is non-perturbative, in that it involves merely optimising the geometry of a molecule with an externally applied electric field and measuring the change in dipole moment associated with the field. There is the slight drawback that a polar molecule must be held fixed in some way if the polarisability at an angle to the dipole moment is to be measured, as the molecule will otherwise rotate to bring its dipole moment towards the direction of the applied field, but when measuring the polarisability along the axis of the moment, or that of a non-polar molecule, this constraint is not necessary and the molecule can be allowed to relax completely.

The polarisability of a molecule is a much more sensitive function of the geometry than the dipole moment, as can be seen if we consider the case of hydrogen fluoride again. The components α_1 and α_2 of the polarisability correspond to changes in the two components of the dipole moment, those parts due respectively to charge separation between the atoms and to polarisation of the bond itself (as in table 5.3). For reference, it is mentioned here that a change in dipole moment of 1 debye per atomic unit of field corresponds to a polarisability volume of $0.0584\text{\AA}^3$.

Table 5.5 Polarisability of HF, as a function of bond length

Bond length (Å)	α_1	α_2	Total α (Å ³)
0.90	0.32	-0.02	0.30
0.95	0.38	-0.02	0.36
1.00	0.44	-0.02	0.43
1.00*	0.57	-0.05	0.51
1.05	0.51	-0.02	0.50
1.10	0.59	-0.01	0.58

* allowing the molecule to relax. The equilibrium bond length in HF is calculated to be $0.99985\text{\AA}$, and this increases by approximately $3\text{\AA}$ per atomic unit of field for small fields.

It is clear that that part of of a molecule's polarisability due to the polarisability of the interatomic bonds themselves is insignificant within the CNDO approximation, and that the important term arises from the movement of charge between the two atoms. Allowing the molecule to distort may make a significant contribution to the molecular polarisability when the molecule is already highly polar (as in this case) or when the effective force constant preventing distortion is small, which might be the case in some biological molecules.

The success of CNDO in making quantitative predictions of molecular polarisabilities has not been great, however, and the reason appears to be due to the failure to treat bond polarisabilities in a satisfactory manner. This is principally a consequence of using only a valence basis set; studies by Davies (1969) of the effect of including 2p orbitals on hydrogen atoms lead to slightly improved results, but the correlation with experimental values is still, at best, tenuous. The principal values of the polarisability tensors of various molecules are tabulated below.

Table 5.6 Theoretical and experimental molecular polarisabilities ($\text{\AA}^3$)

		CNDO(1)	CNDO(2)	CNDO(3)	<i>Ab initio</i> (4)	Experiment(5)
H ₂	(α_{xx})	0.21	1.60	0.46	1.293	0.934
	(α_{yy})	0.0	1.20	0.0	0.801	0.72
N ₂	(α_{xx})	1.10		1.64	4.67	2.38
	(α_{yy})	0.40		0.82	1.27	1.45
HF	(α_{xx})	0.32	0.63	0.51	0.791, 0.859(6)	0.96
	(α_{yy})	0.03	0.22	0.03	0.364, 0.623(6)	0.72
C ₂ H ₄	(α_{xx})	2.40	4.08	2.55		5.61
	(α_{yy})	1.10	2.86	1.15		3.59*(3.96(7))
	(α_{zz})	0.50	1.77	0.46		3.59*(3.38(7))
C ₂ H ₆	(α_{xx})	1.26	3.78	1.49		5.48
	(α_{yy})	1.23	3.76	1.40		3.97

- (1) Davies (1969)
 - (2) Davies (1969), with the inclusion of 2p orbitals on the hydrogen atoms
 - (3) Self-consistent calculations (this thesis)
 - (4) Kolker and Karplus (1963), except where stated
 - (5) Landolt and Börnstein (1951), except where stated
 - (6) Stevens and Lipscomb (1964)
 - (7) Derived using the empirical bond polarisabilities given by Denbigh (1940)
- * assuming rotational symmetry

It is clear that there is a significant improvement to be had in using an *ab initio* method and a larger basis set; both sets of authors using this method obtained results in much better agreement with theory than the CNDO results, except in the case of the polarisability of N₂ along its axis (the axes are defined such that the molecular axis is the x axis, and that the ethene molecule lies in the x-y plane). The basis sets they use are substantially larger than the STO valence basis set used here.

In particular, the CNDO results are very poor when describing the off-axis polarisabilities; as was mentioned before, CNDO only really accounts for polarisabilities due to physical charge separation, and clearly this is not a possibility perpendicular to a bond.

However, the possibility of using CNDO to predict molecular polarisabilities should not be entirely excluded; although the values it predicts are too low, the underprediction is fairly consistent, and certainly sufficiently regular as to allow a reasonable prediction of the experimental value. If we look at the mean polarisabilities of a range of organic molecules, we can see that the underprediction leads to theoretical values that are between 24% and 33% of the experimental results in all but one case.

Table 5.7 Mean polarisabilities ($\text{\AA}^3$)

	CNDO	Experiment ⁽¹⁾	Ratio CNDO:Expt.	.
NH ₃	0.64	2.26	0.29	
HCN	0.84	2.59	0.32	
CH ₄	0.63	2.60	0.24	
CCl ₄	3.02	10.50	0.29	
C ₂ H ₂	0.91	3.33	0.27	
C ₆ H ₆	4.14	10.32	0.40	
C ₂ H ₄	1.39	4.26	0.33	
C ₂ H ₆	1.43	4.72	0.30	

(1) Landolt and Börnstein (1951)

5.5 VIBRATIONAL FREQUENCIES

It should be made clear at the outset that using CNDO to calculate the normal mode frequencies of a molecule is rarely going to be the optimal method. Methods using valence force potentials exist (for a review of the use of valence force potentials, see Allinger 1976), and the force constants used therein have been well parametrised to fit existing data, resulting in the ability to generate an accurate set of theoretical frequencies for most molecules.

In certain special cases, however, it will not be possible to use valence force potentials to describe the molecular vibrations. One such case is the treatment of vibrations in a charged or electronically excited state (since the bond orders, and hence the force constants, will change on excitation or charging), and another is the study of conjugated polymers. Although some computer programs using valence force potentials can handle systems with conjugated π -electrons, they mostly do so by calculating a bond order for each bond (within Hückel theory) and using an empirical bond order: force constant relationship to derive a force constant. This fails properly to take into account electron-phonon coupling, however, and is

thus expected to overestimate the frequencies of the Raman-active phonons in PA (the question of how electron-phonon coupling affected this frequency within the SSH model was considered in §§3.2 and 3.3). Using CNDO to predict these frequencies should overcome this problem, and these calculations will be performed in §6.6.

The calculation of vibrational frequencies within CNDO is a problem that has been studied by Pulay (1969, and a number of subsequent papers), who calculated force constants by a double differentiation process. Performing both differentiations analytically is not feasible (this was remarked in §4.1) and performing them both numerically is immensely time-consuming (although Mori and Kurihara (1988) have recently studied the localised modes around a soliton in t-PA within the MNDO approximation by performing both differentiations numerically), so Pulay suggested performing the first differentiation analytically and the second numerically. Calculation of a complete force constant matrix by this method requires $3N$ total energy calculations, and for small molecules this presents no problem.

For large molecules, and particularly when we only require the frequencies of certain specific modes, it will be quicker to use the molecular dynamical method of chapter 4 to allow the molecule to vibrate in real time, and find the frequencies of the normal modes by Fourier transforming this vibration. The details of this method are outlined here, and it is applied to a few small molecules in order to compare the frequencies obtained with experiment, but it should be stressed that, for molecules of the size considered in this section, the method of Pulay is more appropriate; only for large molecules does the real time method lead to significant savings in computational time.

The modes whose frequencies we require can be selected by careful choice of the initial geometry used. To take a simple example, to find the frequency of the symmetric C-H stretch (the *breathing mode*) in methane requires a symmetric initial geometry, with the C-H bonds all slightly stretched. The

total length of time over which the molecule must be allowed to vibrate depends on the precision to which we want the frequency, and the choice of time step involves a trade-off between the extent to which too large a time step will degrade the harmonic motion of the system and the extra number of steps required if the time step is too small. A time step of 1 unit (where the program's natural unit of time is m_p atomic units, or 1.036fs) is in general found to be suitable.

The example of the breathing mode in methane was used to illustrate the method. The molecule was allowed to vibrate for 200 time steps, and this means that values of the Fourier transform can be calculated at frequency intervals of 0.031 units (boundary conditions dictate that the frequency used for the transform must take the form $2n\pi/(N+1)\tau$). One unit of frequency corresponds to 5118cm^{-1} , so the separation between successive frequencies is approximately 160cm^{-1} . By simply noting the position of the peak, the frequency of the mode can be obtained to $\pm 80\text{cm}^{-1}$, which may be good enough for our purposes but can be improved significantly by looking more closely at the Fourier transform (Fig. 5.2) in the following manner.

Define an effective Fourier transform $F(\omega)$ by:

$$F(\omega) = \sum_n f(t_n) \cos(\omega t_n)$$

Then, if we replace the summation by an integral and assume that the displacement $f(t)$ takes the form $A \cos \Omega t$, we get (for $\omega \approx \Omega$):

$$F(\omega) \propto 1/(\omega - \Omega)$$

This changes sign as the estimated frequency ω passes Ω , and the ratio of the peak heights at either side of this sign change can give us the actual frequency Ω to much better precision than before. If we use ω_m to represent $2m\pi/(N+1)\tau$, and choose m such that Ω lies between ω_m and ω_{m+1} , then we have:

$$\frac{F(\omega_m)}{F(\omega_{m+1})} = \frac{\omega_{m+1} - \Omega}{\omega_m - \Omega} \quad (5.1)$$

The measured peak heights of Fig. 5.2 are -0.98 and 5.95 respectively at

$\omega=0.911$ and 0.942 , so the frequency of the vibration is calculated to be 0.938 units, equivalent to 4800cm^{-1} (without this correction, we would have estimated 4825cm^{-1}). This value is precise to better than $\pm 10\text{cm}^{-1}$.

Sometimes the atomic motion is slightly damped, however, and the resulting Fourier transform is not as sharp as that of Fig. 5.2. It is still desirable to know the normal mode frequency to the same precision, however, and how this may be done is illustrated for the case of formaldehyde (CH_2O). An initial state with the antisymmetric modes excited was used, and the resulting Fourier transform is shown in Fig. 5.3. Assuming that the atomic displacement now takes the damped form:

$$f(t) = A \cos \Omega t \cdot e^{-kt} \text{ (with } k \text{ small)}$$

it is now easy to repeat the calculation of $F(\omega)$, and the result is (again, for $\omega \approx \Omega$):

$$F(\omega) = S \frac{(\omega - \Omega) + Ck}{(\omega - \Omega)^2 + k^2} \quad (5.2)$$

where S is a constant and $C = \tan(\Omega \tau (N+1)/2)$. There are essentially four unknowns in this expression, as C varies so quickly with Ω that it must be treated as an independent quantity. However, it is a trivial matter to fit the observed $F(\omega)$ values to a curve of this form, and even a fit by eye can lead to a value of Ω precise to better than 10cm^{-1} . In Fig. 5.3, the lines are fits by eye, and the calculated vibrational frequencies are 1290cm^{-1} and 4875cm^{-1} respectively.

Comparison between vibrational frequencies calculated using this method and their experimental values confirms that the theoretical values are, without exception, too large. This is in agreement with the well-known result that CNDO overpredicts force constants by a factor typically between 2 and 3 (see e.g. Sadlej 1985, table 5.4, Pople & Beveridge 1970, table 4.1b). Just as in the study of polarisabilities, however, the observation of an apparently systemic overprediction means that we can to some extent allow for it and adjust our calculated values accordingly. By examining the extent of this overprediction in a few sample cases (table 5.8) we can

obtain an estimate of the factor by which the frequency of a vibration in which we are interested will be overpredicted. In the main, the values of table 5.8 fall in the range 1.54 to 1.73, with the C-H bending mode values substantially lower and the C-C stretching mode values rather higher. They are shown in diagrammatic form as fig. 5.4. We will in the next chapter be interested in the Raman-active modes of polyacetylene, and it would not seem unreasonable to expect the overprediction to be somewhere near the top end of the overprediction range. Bear in mind that we do not require an accurate estimate of the Raman frequency, but rather an idea of whether CNDO is able to account for the electron-phonon coupling, which reduces the bare frequency of 1900cm^{-1} to the observed value of 1474cm^{-1} , so an uncertainty of even 100cm^{-1} should not affect the interpretation of the results.

Table 5.8 Vibrational frequencies (cm^{-1})

	Observed ⁽¹⁾	Calculated	Ratio calc.:obs.
HCN bend	712	1100	1.54
C≡N stretch	2089	3320	1.59
C-H stretch	3312	5190	1.57
CH ₂ O symmetric bend	1503	1610	1.07
antisymmetric bend	1280	1290	1.01
symm. C-H stretch	2780	4810	1.73
antisymm. C-H str.	2874	4875	1.70
C=O stretch	1744	2880	1.65
CH ₄ breathing mode	2914	4800	1.65
antisymm. C-H str.	3020	4950	1.64
C ₂ H ₄ C=C stretch	1623	2640	1.62
C ₂ H ₆ C-C stretch	993	2190	2.20
CH ₃ CN C-C stretch	918	1840	2.00

(1) Herzberg (1945)

5.6 BIOLOGICAL MOLECULES

To understand the behaviour of many important biological molecules it is necessary to have knowledge both of their electronic structure and of their shape. Most biologically important molecules, however, are rather large, and self-consistent studies are rare; studies have tended to involve either wave function calculation at fixed geometry or geometry optimisation by a valence force potential method. On a larger scale, models which pack molecules into substrates assuming that both components are rigid have also been examined. For a brief review, and a more detailed presentation of the results of this section, see Stoneham and Wallace (1989).

None of these three methods is entirely satisfactory. Calculating the wave functions at a non-optimised geometry, which may have been selected in a fairly arbitrary manner, seems unsatisfactory when the shape of the molecule is so crucial, and the question of how the shape of the molecule changes on excitation or ionisation is ignored altogether. Using a valence force potential method to find the optimised geometry, coupled with a quantum chemical method to find the wave functions, remedies the first problem but leaves the second untouched, and the packing model fails to account for the flexibility of many molecules.

There is the additional consideration that modelling of a receptor, even during the self-consistent calculation, is extremely desirable, and the simplicity of the energy minimisation process used in this thesis means that it is ideally suited to this problem.

As a sample molecule, serotonin (5-hydroxytryptamine) was chosen for a number of reasons: it is of moderate size (25 atoms) but considerable importance (Page 1957, Jacobs 1987), and is known to bind to at least three distinct receptors. In addition, it is related to a number of other molecules, such as bufotenine and lysergic acid diethylamide (LSD), which are also of considerable interest biologically. In this section, we will examine the behaviour of serotonin under various conditions, and hope to

obtain an idea of which parts of the molecule are important under which conditions.

The structure of serotonin is shown in fig. 5.5. Its ground state geometry is not definitively known, since the planar form observed in crystals of cationic serotonin is predicted to be unstable in isolation, and merely an artefact of the crystallisation (Port and Pullman 1974, Kang *et al.* 1973). Calculations within the CNDO method agree with these authors that the non-planar form of fig. 5.6 is the stable form in isolation.

The geometry of serotonin has also been calculated in charged and excited states, and the results obtained suggest that it is the behaviour of the side chain, and its interaction with the hydrogen atom labelled 24 in fig. 5.6, that is primarily of interest. On excitation, the side chain closes up towards the indole ring and the C-H bond length between atoms 8 and 24 increases substantially (by about 0.2Å). Charge (about 0.2|e|) is also transferred from carbon atoms 7 and 8 onto the nitrogen atom 11, so the overall effect is the partial transfer of a proton from the indole ring onto the amine group. The benzene ring is practically unaffected by excitation.

The effects of charging the serotonin molecule are less exciting, but it is still observed that the side group does move significantly. If a positive charge is added to the system, the side group closes up towards the indole ring and there is some slight movement of hydrogen atom 24 towards the amine group; if an electron is added, the reverse is the case and the benzene ring, which is where most of the charge is stored in this case, expands slightly (a similar affect will be observed in polyacetylene in the next chapter). A positive charge, on the other hand, is mostly stored on the nitrogen and hydrogen atoms of the side chain.

It appears from the calculation on the photoexcited state that the hydrogen atom labelled 24 and attached to the indole ring is significantly acidic. If we protonate the primary amine group at the end of the chain, therefore,

the resulting repulsive interaction should lead to the chain opening out, away from the indole ring, and this is indeed observed when the calculation is performed.

A simple calculation representing the interaction between serotonin and a one dimensional model receptor was also carried out. The receptor was modelled by a force field consisting of a potential minimum along the line drawn in fig. 5.7, with an infinite barrier along the dotted line. Only the non-hydrogenic atoms were considered, with all hydrogens being anchored to their host atoms; this removes the high-frequency vibrational modes from the calculations and thus enables the use of a larger time step. It should be emphasised that this was only an example calculation (since the detailed examination of serotonin-receptor interaction is beyond the scope of this thesis) but it can easily be seen how the geometry of the molecule is affected. Atoms 1, 2 and 3 were held fixed in the plane of the ring system, to prevent the entire molecule from rotating to lie flat against the potential minimum. The main changes are that the benzene ring has distorted slightly, and that the side chain has again closed up very significantly. This is further evidence for the theory that the behaviour of the side chain is of primary interest in serotonin.

5.7 FURTHER AREAS OF APPLICATION

The self-consistent geometry optimisation process described here can be applied to the study of any system where electron-lattice coupling is important, subject to the condition that it be well described by a semi-empirical method similar to CNDO. This enables both the study of a wide range of classical defect theory and the examination of the behaviour of molecular systems in ground, excited or charged states.

Two further features of this method lend it to a number of additional areas of study: firstly, its molecular dynamical nature means that chemical reaction pathways can be investigated; molecules can even be pushed towards

each other in order to allow a kinetic barrier to be overcome or to simulate an applied pressure. Secondly, the flexibility of the method means that externally applied effects can be considered; the treatment of a receptor molecule when considering the behaviour of serotonin in §5.6 is just one form of external constraint which can be examined. Another area of study which has been suggested (A.P.Sutton, private communication) is the use of the facility to apply a non-uniform electric field to the system under investigation in order to consider how the geometry of a biological molecule might be affected by the tip of a scanning tunnelling microscope, and thus to what extent such a method of measuring a molecule's structure would be useful.

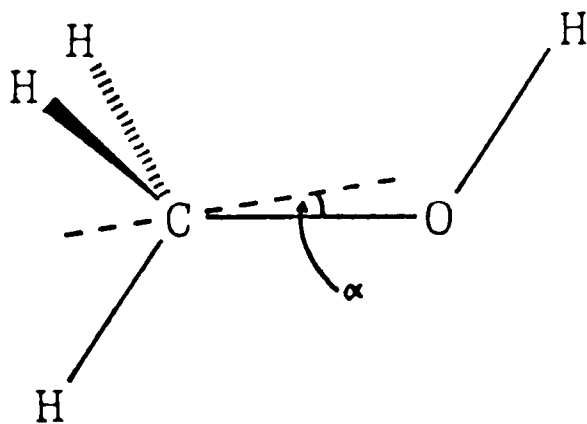


Fig. 5.1 Geometry of methanol (see table 5.1, p. 5.3). Note how the axis of the methyl group is shifted slightly away from the C-O bond.

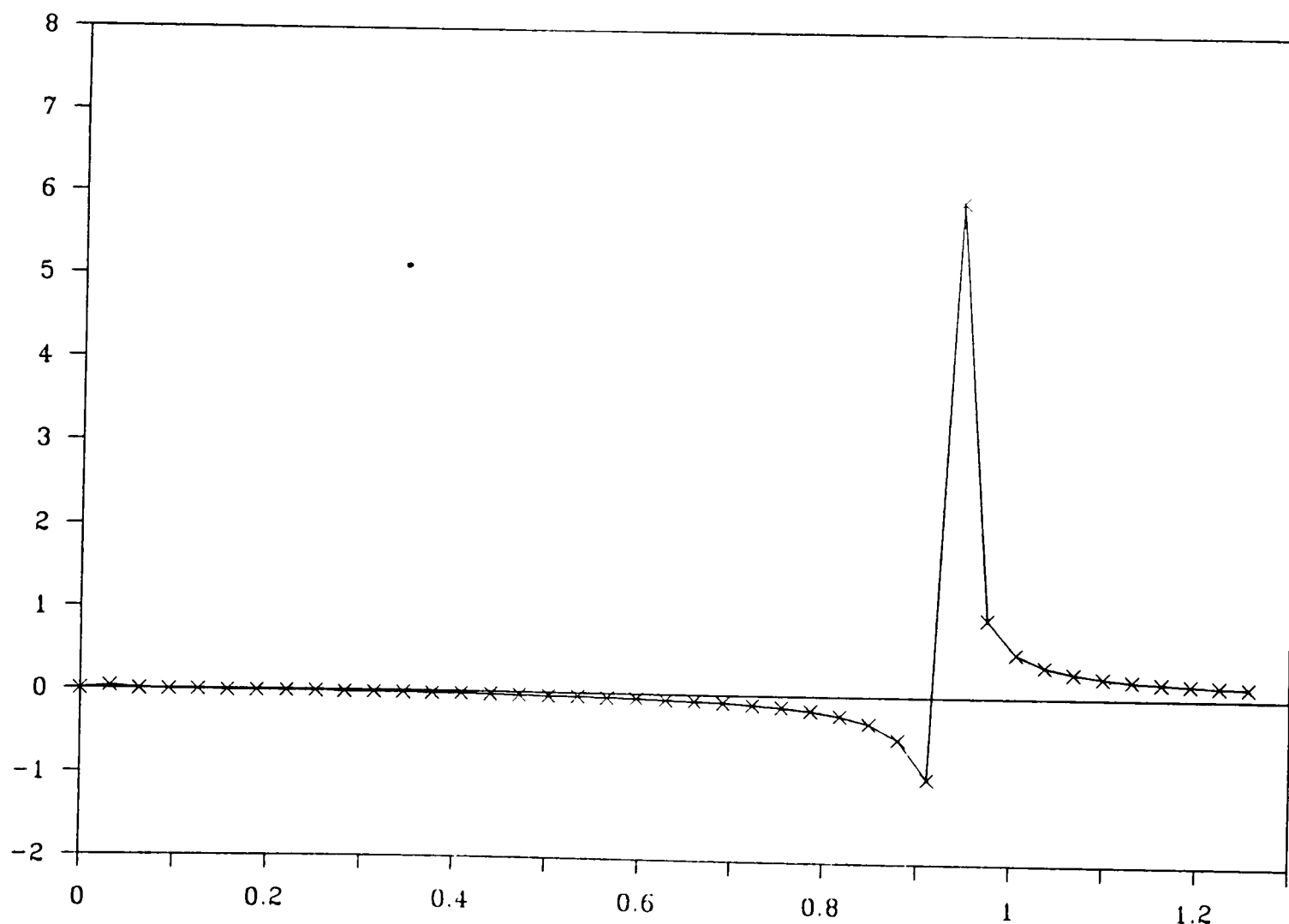


Fig. 5.2 Fourier transform of the C-H bond length in methane, obtained from a dynamical run. The line is merely a guide for the eye. The precision with which the vibrational frequency may be obtained is improved significantly by examining the behaviour of the transform around the peak (see (5.1), p. 5.12). The units of frequency are the program's natural units, where $\omega=1$ represents a frequency of 5118cm^{-1} , so the peak is observed at 4800cm^{-1} .

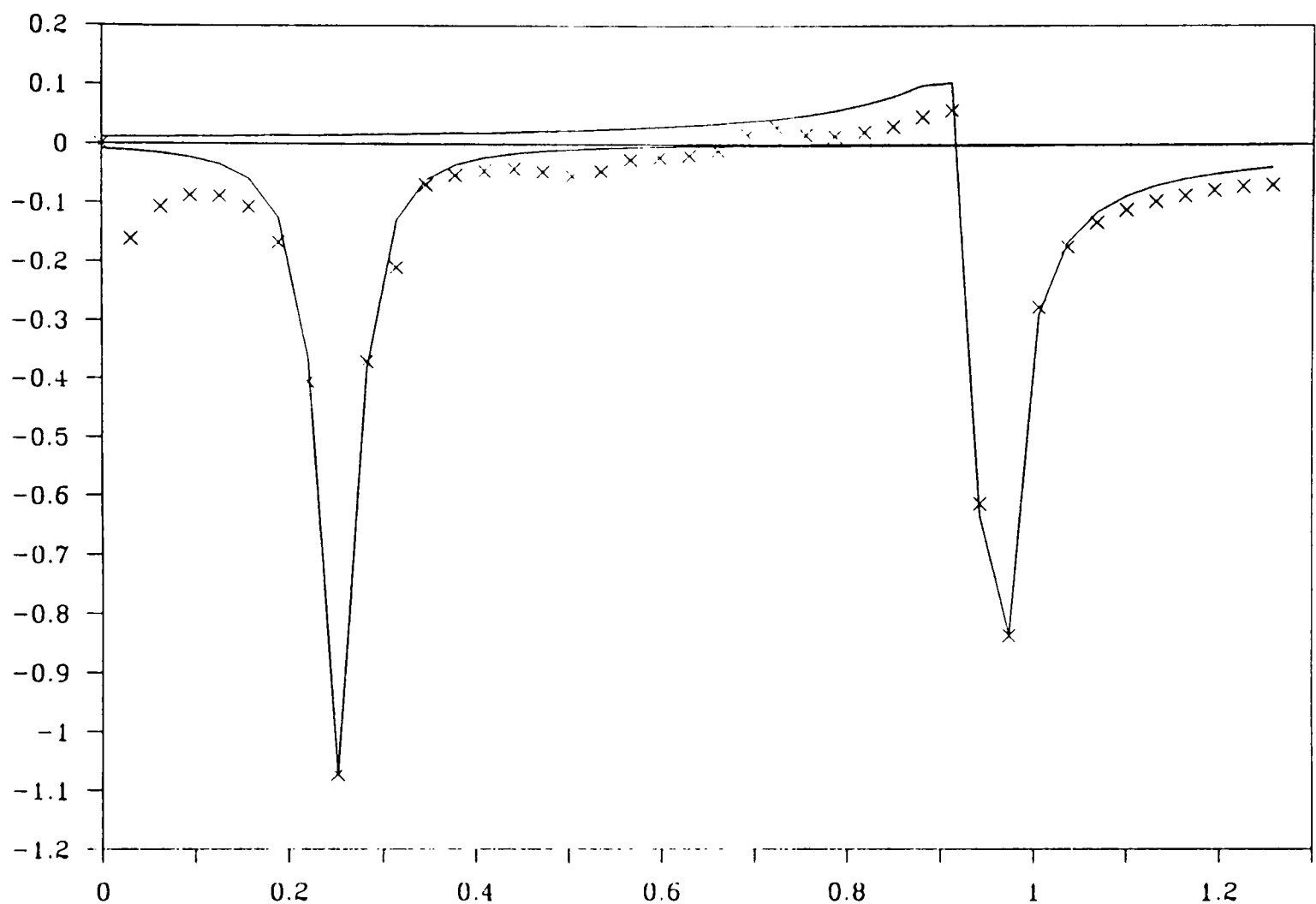


Fig. 5.3 Fourier transform of one co-ordinate of the carbon atom in formaldehyde. The initial conditions were such that only the two antisymmetric normal modes are present. The peaks are not as sharp as those observed for methane in fig. 5.2, but it is still possible significantly to improve the precision with which their positions are calculated. This is done by fitting the observed values to curves of the form (5.2) (p. 5.13); the lines drawn here are fits by eye for each of the two peaks. The units of frequency are the same as those of fig. 5.2, and the peaks occur at 1290cm^{-1} (antisymmetric bend) and 4875cm^{-1} (antisymmetric C-H stretch).

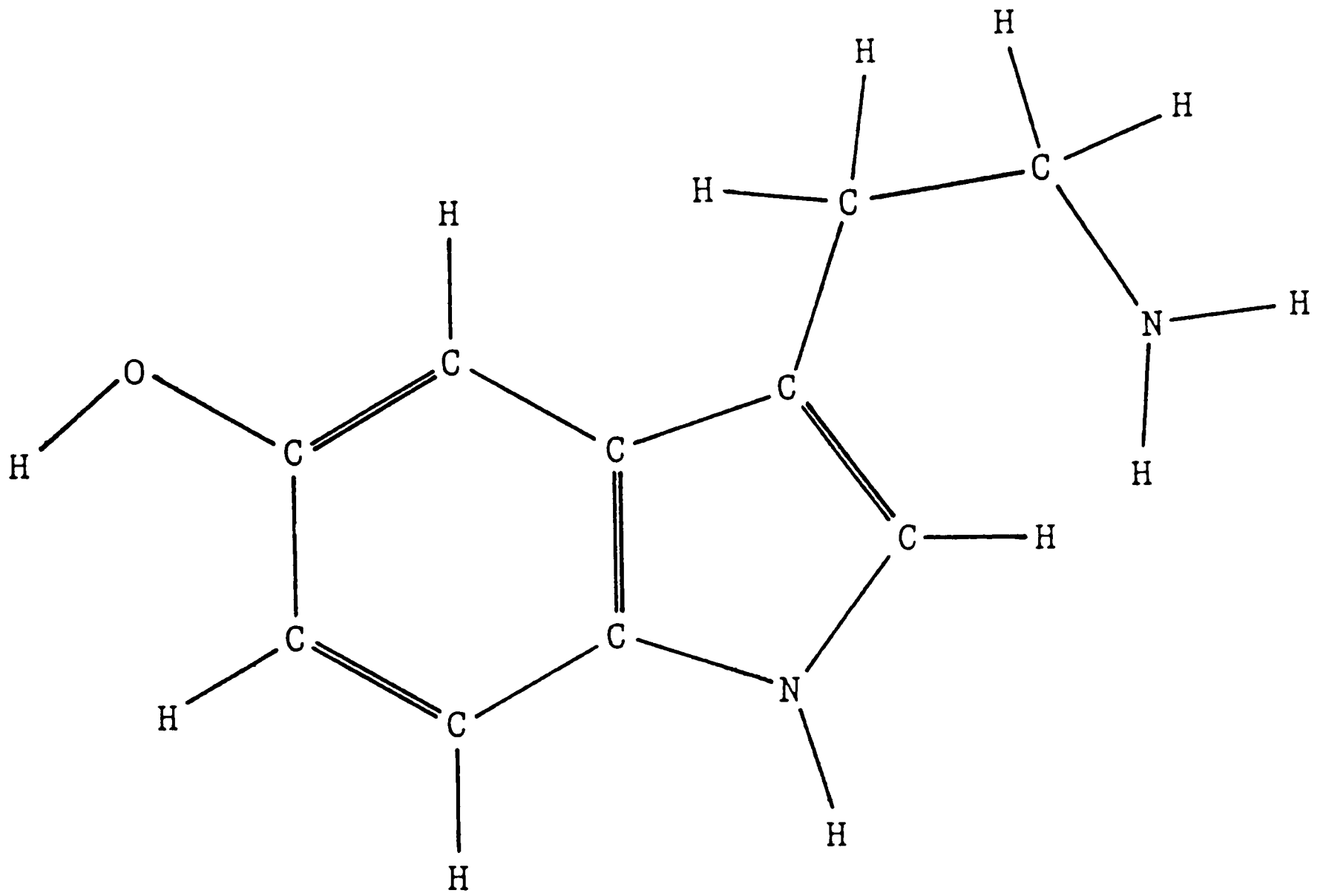


Fig. 5.5 Structural formula of serotonin.

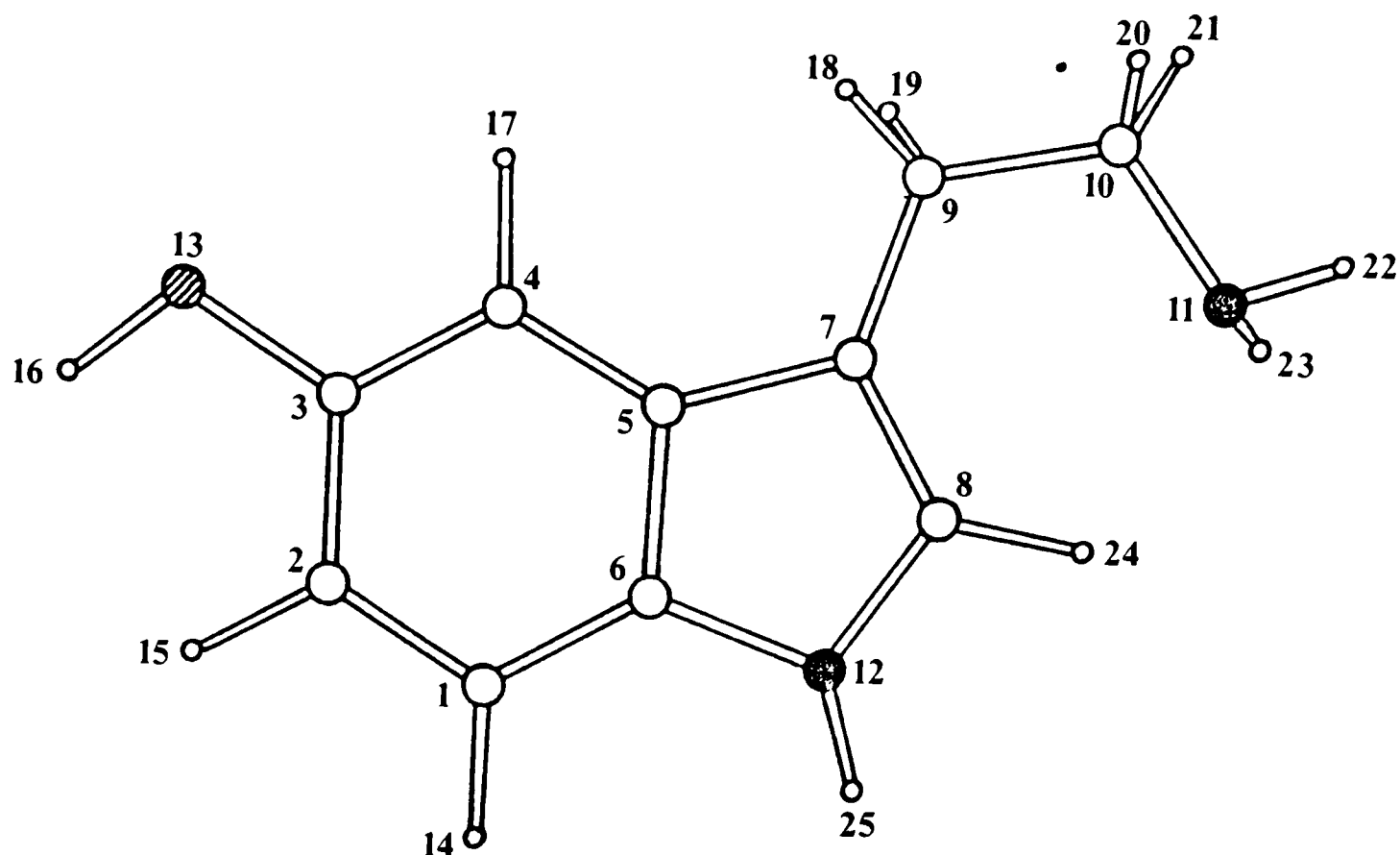


Fig. 5.6 Ground state geometry of serotonin, as calculated by CNDO. The side chain is predicted to lie out of the plane of the ring system, in agreement with previous calculations.

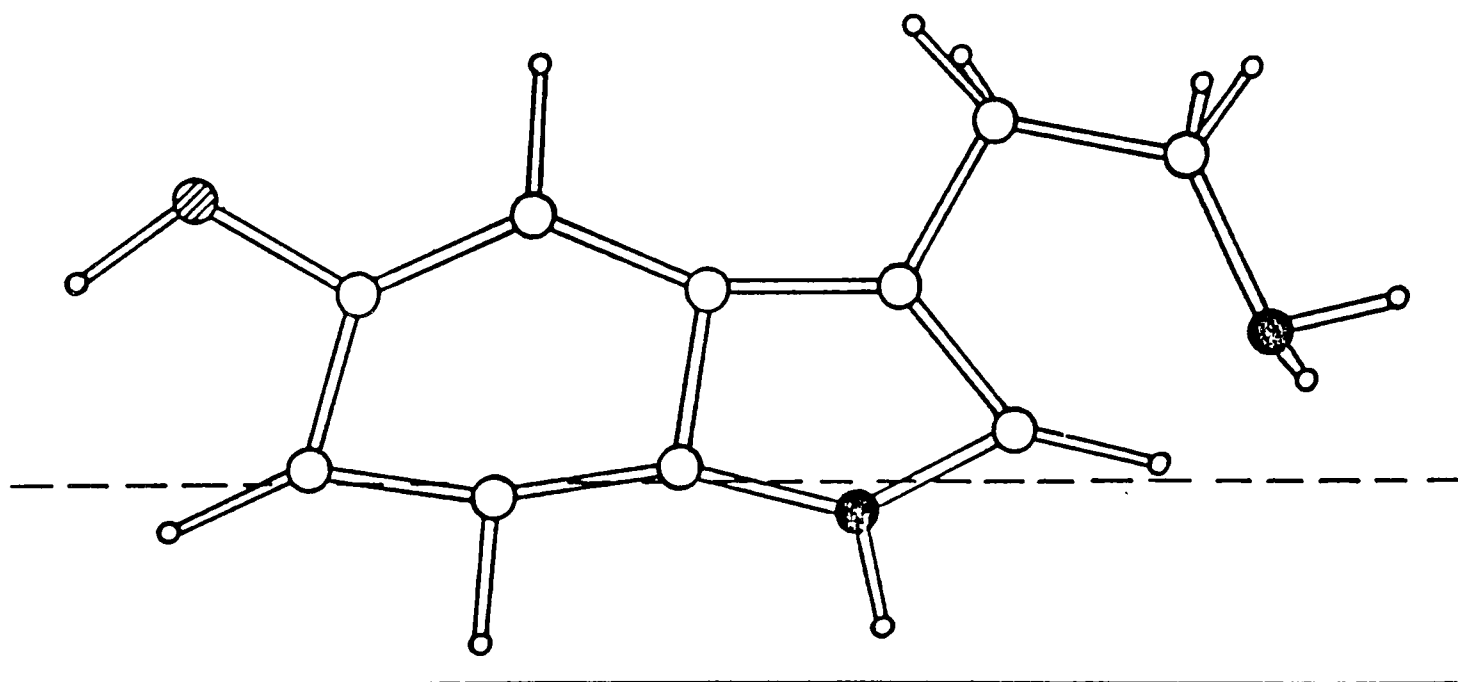


Fig. 5.7 Geometry of serotonin, with a model receptor present. The model consists of a force field, applied only to atoms other than hydrogen, such that there is a potential energy minimum in the vertical plane corresponding to the solid line, and an infinite barrier in the plane corresponding to the dotted line. The molecule was prevented from rotating to lie flat within the plane of the energy minimum by preventing certain atoms in the ring structure from moving in the vertical direction. Note the significant distortion of both the six-membered ring and the side chain that is caused by this model.

6.1 INTRODUCTION

The method outlined in chapter 4 is applied in this chapter to the study of defects in the two polyacetylene isomers, in polythiophene and in polydiacetylene. At the end of the chapter the behaviour of β -carotene is also discussed briefly. Previous authors have used semi-empirical methods, in particular MNDO, to calculate defect geometries in t-PA, but have obtained significantly different results even when using the same method. Here CNDO, which has had a good deal of success in calculating molecular geometries in the past, is used in a further attempt to find self-consistent defect geometries and to calculate wave functions more able to account for experimental observations than those produced by the SSH model. The nature of the doping process is also studied, in a manner which makes no empirical assumptions beyond those of the CNDO model itself.

In addition to these static calculations, the dynamical behaviour of polyacetylene is modelled in order to study three effects: the way in which injection of a soliton at the end of a t-PA chain results in the defect moving into the chain interior, the mobility of a charged soliton in t-PA and the important and much studied case of the creation of an electron-hole pair (modelled in this chapter by the behaviour of the lowest triplet state of each isomer). The behaviour of t-PA on photoexcitation, and in particular its dynamical behaviour, has aroused much interest because of the possibility of formation of a form of dynamical defect known as a *breather* (Bishop *et al.* 1984), which has been postulated as the species responsible for the 1.35eV peak in the photoinduced absorption spectrum of t-PA. Previous studies have used methods based on extended Huckel theory, including the SSH model, to predict the possible existence of no fewer than three types of breather, each of which may be formed if the energy injected into the system is appropriate (Wang and Martino 1986).

The possibility of the existence of breathers in c-PA has not previously been studied, possibly because of the absence of a satisfactory model. The dynamical nature of the code used here, however, coupled with its flexibility and its high speed of calculation, means that it is ideally suited to investigations of this type.

6.2 GROUND STATE GEOMETRIES

POLYACETYLENE. The ground state geometries of t-PA and c-PA were found by examining molecules of t-C₄₈H₅₀ and c-C₃₂H₃₄. These were observed to be sufficiently large that end effects could be neglected when dealing with the bond lengths and angles in the central region of the chain; the ground state dimerisation curve of the c-PA model molecule is shown in fig. 6.1, to illustrate the short range over which end effects may need to be considered (the equivalent range in t-PA is very similar). The results, in terms of bond lengths and angles, are summarised in table 6.1 below. c-PA was predicted to occur in the cis-transoid isomer (see chapter 1), in agreement with all other theoretical and experimental studies.

Table 6.1 Ground state geometries of the polyacetylene isomers

	trans isomer	cis isomer
C-C bond length	1.424Å	1.428Å
C=C bond length	1.336Å	1.338Å
Dimerisation	0.084Å	0.090Å
C-H bond length	1.119Å	1.119Å
C=C-C angle	123.4°	124.4°
C=C-H angle	116.8°	118.9°

These results are in good agreement with experimental observations of the dimerisation amplitude (Yannoni and Clarke 1983) and, except in the predicted C=C-H bond angle, with the MNDO results of Boudreaux *et al.*

(1983): these authors predicted that the C-H bond would be inclined towards the C-C single bond by 4.4° , rather than towards the double bond as found here. This discrepancy should not significantly affect the reliability of the results of this chapter, however.

POLYTHIOPHENE. Unlike c-PA, polythiophene (PT) is predicted to exist in the trans-cisoid isomer (fig. 6.2), and the two C-C single bonds are no longer equivalent. The length of the C-C bond joining adjacent thiophene rings is predicted to be rather larger than that of the C-C bond within a ring, indicating how the sulphur atoms within the thiophene rings are able to attract the p_z electrons, thereby reducing the extent of conjugation between rings. The remaining bond lengths in polythiophene are similar to their equivalents in c-PA:

C-C 1.428Å⁽¹⁾, 1.441Å⁽²⁾ C=C 1.355Å C-S 1.929Å C-H 1.119Å

(1) within a thiophene ring (2) between rings

The bond angles, however, are found to lie much closer to 120° than in either of the PA isomers, with the two inequivalent C-C=C angles both approximately 121.5° . It was mentioned in §2.4 that the trans-cisoid isomer might be expected to display a slightly smaller bond angle than the cis-transoid.

POLYDIACETYLENE. The structure of a general polydiacetylene is shown in fig. 6.3. The R and R' groups may take many forms, with commonly studied polydiacetylenes including PDA-TS, with $R=R'=\text{CH}_2\text{OSO}_2\text{C}_6\text{H}_4\text{CH}_3$, which is available in crystalline form, and PDA-1OH, with $R=\text{H}$, $R'=\text{OH}$, which forms less good crystals.

While the polymerisation of acetylene takes place in solution, and it can be assumed that there are sufficient species available to allow for an easy termination, polydiacetylenes are polymerised in the solid state from the monomer crystals (Wegner 1969) and the mechanism by which termination of the polymerisation takes place should not really be overlooked, since it will affect the boundary conditions we impose. Sixl et al. (1985)

considered oligomers of polydiacetylene itself ($R=R'=H$) within a Hückel-type model, and did not concern themselves with the termination process, leaving the oligomers in a form where the terminating carbon atoms were each left with two unpaired electrons. It is inconvenient to have to perform numerical defect calculations when there already exist unpaired electrons at the chain ends, and the termination mechanism of fig. 6.4 is proposed to avoid this problem. This form of intramolecular insertion is typical of carbenes; see e.g. Isaacs (1974) p. 387.

Evidence in support of this theory concerning the termination mechanism is the fact that the polydiacetylenes which form the best crystals tend to have $R=R'=CH_2R''$ (e.g. PDA-TS above) (Sandman and Chen 1989). Accordingly, the conjugated section of a diacetylene chain is predicted to end with a double bond and to contain $4n+2$ carbon atoms; a naive model which ignored the termination problem would assume that the chain contained $4n$ carbon atoms.

In order to reduce the number of atoms it was necessary to include in the calculation, the side group chains were ignored and replaced with hydrogen atoms for all other purposes, so that sample molecules of PDA took the form $C_{4n+2}H_{2n+4}$, except in the special case within §6.4 where an asymmetric chain was required.

The bond lengths in polydiacetylene were found to be:

C-C	1.412Å	C=C	1.339Å	C≡C	1.223Å
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showing how, just as in the case of the polyacetylenes, conjugation has reduced the difference in bond lengths from that predicted by the simple chemical picture; CNDO calculates the equivalent bonds to be 1.46Å, 1.31Å and 1.20Å respectively in a non-conjugated environment.

6.3 DEFECT STATES IN POLYACETYLENE AND POLYTHIOPHENE

SOLITONS. Fig. 6.5 shows the calculated geometries of a soliton in t-PA, using a molecule of $C_{49}H_{51}$ as a model. Both the (positively) charged and

uncharged geometries are shown, and the resulting distortions are fitted well by curves of the form $d_0 \tanh(x/\ell)$. In the charged case, the best value of ℓ is found to be 8.1 lattice units; the uncharged soliton has $\ell=6.5$ units. As in the simpler treatment of electron-electron interaction represented by the Hubbard U (see §3.6), the width of a charged soliton is predicted to be slightly greater than that of a neutral soliton.

These results compare fairly well with both the SSH value ($\ell=7$) and the results of Mori and Kurihara (1988), who used the MNDO method to calculate the geometry of a charged soliton and found $\ell \approx 6$, again with a good fit to a $\tanh$ function. Although Boudreaux *et al.* (1983) also used MNDO, they found very different results from Mori and Kurihara, with a distortion pattern bearing little resemblance to a smooth $\tanh$ curve but having half widths of about $\ell=3$ (uncharged or negatively charged) or $\ell=5$ (positively charged). The reason for the complete disagreement between these two sets of authors is not clear, especially since they agree on the ground state dimerisation amplitude to three decimal places.

By displaying how the charge associated with a charged soliton is stored along the chain (fig. 6.6), we can obtain two important results. Firstly, it is clear that a good deal of the charge (approximately 20%) is actually stored on the hydrogen atoms, rather than the entire charge resting on the carbon atoms of the chain, as is assumed by the SSH model. Note how the charge stored on each carbon atom alternates along the chain; the SSH model predicts that each alternate atom is uncharged, but CNDO predicts that alternate atoms will actually bear *opposite* charge to the charge of the defect itself. This at first sight somewhat surprising result is in agreement with experiment; the way that the charge is distributed along a chain has been measured by means of X-ray photoelectron spectroscopy (XPS) by Sasai and Fukutome (1986). The contribution of the hydrogen atoms to the charge storage does not display this alternation, however, indicating that it is peculiar to the π -bonded system.

The study of a doubly charged molecule of $C_{48}H_{50}$ (Fig. 6.7) provides evidence in support of the assertion that the bipolaron is unstable in t-PA, a result also predicted by the SSH model. Two well separated solitons are observed, and the distortion pattern shown in the diagram is fitted to a pair of tanh functions. Again the fit is a good one, although in the centre of the chain the distortion is actually greater than the sum of the tanh curves, showing how the solitons are physically repelling each other.

POLARONS. The lattice distortion around a polaron in t-PA reproduces the SSH and MNDO results less well, with the distortion predicted by CNDO being rather greater than that predicted by either of the other methods. Fig. 6.8 shows the CNDO prediction for the geometry of a polaron; the fitted curve corresponds to a distortion represented by the difference of two tanh functions, with widths 5.1 units and separation 9.4 units. For comparison, the distortion predicted by SSH was shown in Fig. 2.5. Boudreaux *et al.* predicted distortions similar to the SSH results, with the minimum dimerisation being 0.05Å in the positive polaron and 0.03Å in the negative polaron (CNDO predicts a negligible difference between the distortion patterns of the two polarons).

The extent of distortion in a polaron in c-PA is slightly less than in t-PA, due to the absence of ground state degeneracy. Fig. 6.9 shows that it is still substantially greater than that predicted by the extension of the SSH model to represent c-PA (see fig. 2.15); the curve is again a fit to two tanh functions, this time of width 5.3 and separation 8.4 units, indicating that the polaron is slightly more localised, as well as less marked, than in t-PA.

In polythiophene, the distortion pattern of a polaron is not smooth (fig. 6.10), since there are two inequivalent C-C bonds, but it is readily seen that the width of the distortion is rather greater than that of the polaron in c-PA, being comparable to the equivalent width in t-PA. This is

in accordance with there being weaker confinement (non-degeneracy) in PT than in c-PA; as was mentioned in §3.7, Vardeny *et al.* (1986) estimated that the confinement parameter as defined by Fesser *et al.* (1983) was approximately 0.27 for PT, compared to 0.7 for c-PA; these correspond to values of about $0.4\text{eV}\text{\AA}^{-1}$ and $1.0\text{eV}\text{\AA}^{-1}$ for the steric parameter of §2.4, using the method of §3.5 to compare the two values.

BIPOLARONS AND EXCITONS. That CNDO predicts a greater distortion than SSH is also true of the bipolaron in c-PA and PT (MNDO results are not available, since Boudreaux *et al.* did not consider materials other than t-PA, or the effects of multiply charging the chains); in the centre of the defect in c-PA the chain is almost in the trans-cisoid form (fig. 6.11), rather than approximately undimerised (fig. 2.17).

The effect of breaking charge conjugation symmetry can be seen by comparing this diagram with fig. 6.12, which shows the distortion pattern of an exciton in c-PA (modelled as the lowest-lying triplet state; CNDO does not consider those terms in the energy which separate singlet and triplet states, so since excited states are difficult to examine in CNDO the equivalent triplet state is used instead). Although the maximum distortion is similar in each case, the distortion within an exciton is much sharper, showing how the bipolaron distortion is broadened by Coulomb repulsion; a sharper distortion corresponds to a more localised wave function, and thus it is energetically favourable for the bipolaron to spread itself out further, in order to minimise its Coulomb energy. This is precisely the same effect that leads to a charged soliton width in t-PA less than that of the neutral soliton.

The results obtained for PT mirror those for c-PA, with the lower level of confinement leading to broader defects: fig. 6.13 shows that the width of a bipolaron is so large that the chain used in the calculation (a chain of seven thiophene rings, i.e. 28 carbon atoms) was too short to contain a bipolaron without the defect being artificially localised by the chain

ends. The exciton distortion pattern (fig. 6.14) again has a similar amplitude but smaller width than that of the bipolaron. Both exciton and bipolaron have a much larger distortion amplitude than that predicted by the SSH model (fig. 2.16).

It should be mentioned at this point that there is some experimental evidence in support of the CNDO results in this last case at least. The distortion due to an exciton in polythiophene has been measured indirectly by Tanaka *et al.* (1984) by means of photoinduced IR spectroscopy; they found that the photoexcited state displayed vibrational modes characteristic of the cis-transoid isomer (the less stable isomer of polythiophene), rather than just of some state intermediate between the cis-transoid and trans-cisoid isomers. The presence of a region of the unstable isomer in the exciton is in accord with the CNDO predictions, rather than the SSH predictions of weaker distortion.

No direct evidence exists concerning the other defect types, but it does not seem unreasonable to suppose that CNDO, having more accurately predicted the distortion pattern for one type of defect, will also prove reliable when considering the other defect types. It will be shown in chapter 7 that the prediction of a much greater distortion than that of the SSH model has important consequences when considering the observed luminescence quenching in c-PA.

Just as in the SSH model, addition of a defect to a polyacetylene chain is predicted to affect the chain length; typically, a defect increases the length of a polymer chain by a few hundredths of an angstrom, with the effect being more marked for the addition of negative charge; a positive bipolaron added to a chain of c-PA actually *decreases* the chain length slightly.

6.4 DEFECTS IN POLYDIACETYLENE

It is not as easy to assign a dimerisation parameter to polydiacetylene as

it is to the polymers with a simple C-C=C-C=C backbone, in such a way that defect-induced absorption patterns will appear as smooth curves. Instead, the extent of the distortion is represented by the change in bond lengths b_n from their ground state values b_n^0 :

$$d_n = (-1)^{n+1}(b_n - b_n^0)$$

The factor $(-1)^{n+1}$ is included so that a distortion which lengthens the multiple bonds and shortens the single bonds around a defect will correspond to a value of d_n which is positive throughout.

Graphs of the distortion patterns of an exciton in PDA are shown in figs. 6.15-6.17. The exciton of fig. 6.15 has been constrained to be centred on a double bond linking two diacetylene units by using a molecule of $C_{34}H_{20}$, i.e. one with an even number of carbon units (note that the molecular dynamical method will not break externally-imposed symmetries), and that of fig. 6.16 to be centred on a triple bond within a diacetylene unit by using the molecule $C_{30}H_{18}$. It is interesting to note that the two excitons are virtually degenerate (the calculated energies are 3.336eV and 3.334eV respectively; although CNDO is primarily designed for the prediction of molecular geometries, and is less good at predicting absolute energies, it is likely that this near-degeneracy is correctly predicted). Bearing in mind that, for a short chain, the energy of a defect such as an exciton will decrease as the chain length increases, the fact that the defect centred on a triple bond in $C_{30}H_{18}$ is predicted to be of slightly lower energy than that centred on a double bond in $C_{34}H_{20}$ is probably a genuine result, although it should be reiterated that the difference in energies is very small indeed.

Using an asymmetric model molecule, $C_{28}H_{16}$, leads to the defect shape of fig. 6.17; although the defect does bear some resemblance to that of fig. 6.16, the difference in energy between the double and triple bond situations for the exciton is so small that end effects are sufficient to push the defect towards the centre of the chain rather than allow it to be

centred on a triple or double bond (despite the exciton being substantially more localised than in polyacetylene). The ordering of energy between the excitons centred at double and triple bonds would agree with the results of Kim *et al.* (1989), who observed polaronic defect states in various polydiacetylenes and postulated that what they called the π' electrons, i.e. the electrons in the $C\equiv C$ π -bond *within* the molecular plane, would help to stabilise the defect at a triple bond.

A similar near-degeneracy between defects centred at double and triple bonds is observed when considering polarons and bipolarons. The distortion patterns of defects centred at triple bonds appear slightly more stable than those centred at double bonds, and these are the cases plotted, but the difference in energy is again very small. The depths of the distortions, plotted in fig. 6.18 for defects centred at triple bonds, are very similar to those of their equivalents in c-PA, but the distortions are again more localised in PDA; this is also in agreement with the predictions of Kim *et al.* (1989).

6.5 DOPING

SSH-based and other empirical models for the study of defects in conjugated polymers are very weak in their treatment of the doping process. It is usually assumed that the only effect of the dopant is to donate a charge to the polymer, although Bryant and Glick (1982) made an attempt to include the potential induced by the dopant into their calculations in a phenomenological manner, without treating the change of shape of the resultant lattice distortion in any more than the simplest fashion. The use of a more general quantum chemical method such as CNDO enables us to examine the doping process in more detail, and the results obtained cast significant doubt on the validity of the usual assumptions.

A sodium atom was placed close to a molecule of t-C₂₄H₂₆ and the system was allowed to come to equilibrium under the action of the forces defined by

CNDO (chapter 4). It was found that the most stable position for the sodium atom was out of the molecular plane and midway between two carbon-carbon bonds, rather than directly over one of them (the relaxation process was deliberately started from an asymmetric configuration to allow for both possibilities).

The resulting distortion pattern is shown in fig. 6.19, in two forms. To calculate the bond lengths, and hence the dimerisation, it is strictly necessary to include the atomic displacement perpendicular to the molecular plane, but the in-plane distortion will still be the dominant term affecting π -electron coupling and the contribution of this term alone is plotted too. The distortion loosely resembles that of a polaron, but on closer examination appears to consist of two parts: a shallow polaronic distortion, over the usual range, with a more marked distortion of a few atoms at the centre of the defect. That the ion is sufficiently close to be interacting with the chain in more than a Coulomb-like manner is seen in fig. 6.20, which shows the molecular distortion perpendicular to the plane; clearly close-range forces are important too, a fact which is borne out by the optimal distance of the sodium ion from the plane being only about $2.5\text{\AA}$, well within the range for which overlap integrals need to be considered.

As well as showing that the interaction between dopant ion and charged chain needs to be considered in a less arbitrary manner than that suggested by Bryant and Glick, these calculations imply that even the assumption of complete charge transfer between the dopant and the chain may be questionable. The total charge stored in the chain by the use of sodium as a dopant is found to be only $0.71e$.

Other dopant ions have also been considered: doping with Li and F leads to qualitatively similar distortion curves, although the smaller size of the Li^+ and F^- ions, and their consequent positioning closer to the chain, mean that those elements of the distortion patterns that are due to short-range

effects are more localised. In each of these cases, furthermore, the amount of charge transferred is much *smaller* than for sodium, with under $0.3|e|$ being transferred in each case. In other words, the application of the simple model of complete charge transfer and interaction via a smooth electrostatic potential is even *less* appropriate for these dopants than for sodium.

6.6 RAMAN FREQUENCIES

The effect of electron-lattice coupling on the dispersion relation of t-PA was examined in §3.3, and it was shown that the frequency of the Raman-active LO phonon was reduced, within the SSH model, from a bare (i.e. uncoupled) value of 1900cm^{-1} to approximately 1270cm^{-1} as a consequence. The observed Raman frequencies in t-PA and c-PA are 1470cm^{-1} and 1540cm^{-1} respectively (Lefrant *et al.* 1979) and we should like to find the frequencies predicted by CNDO, in order to test how well the method can account for the electron-phonon coupling. These frequencies were found by setting up molecules of t-C₂₄H₂₆ and c-C₃₂H₃₄ in states corresponding to excitations of the LO modes, and the frequencies obtained, using the method of §5.5, were 2660cm^{-1} for t-PA and 2680cm^{-1} for c-PA (for reasons of economy of computer time, these values are precise only to $\pm 30\text{cm}^{-1}$). These should of course be scaled down in order to account for the systemic overprediction by CNDO; by comparison with table 5.8 and fig. 5.4, it was estimated that the values would be in error by a factor of about 1.7-1.8, which would lead to scaled predictions of about 1520cm^{-1} and 1530cm^{-1} respectively. Bearing in mind the approximate nature of the compensation process, agreement with experiment seems to be really rather good. For comparison, scaling the calculated frequency for t-PA to the bare frequency of 1900cm^{-1} would require a factor of only 1.4, well below the typical values for overprediction of carbon stretching mode frequencies.

6.7 SOLITON MOTION AND THE SPEED OF SOUND IN t-PA

Su and Schrieffer (1980) studied the effect of setting up a chain of t-PA with a soliton at one end; this is easily done by starting with an odd chain and uniform dimerisation, so the chain ends with a long bond and a localised state associated with it (see fig. 1.5). They used the SSH model but adjusted the parameters so that the defect size was reduced, thereby enabling them to use a smaller chain than otherwise necessary, and found that the soliton moved up the chain with a characteristic velocity similar to the speed of sound c_s in t-PA, which was estimated by Guinea (1984), using the SSH model, to be $1.85 \times 10^4 \text{ms}^{-1}$. The method used here is ideally suited to the repetition of these calculations within CNDO, and the results are shown in figs. 6.21 and 6.22.

Fig. 6.21 measures the speed of sound in t-PA within CNDO, by showing how a pulse travels down a chain of t-PA at a constant speed of approximately 0.3 carbon atoms per time step, although it is significantly attenuated as it travels; the time step used was the program's natural unit of time, which is $\sqrt{m_p}$ atomic units (approximately 1.04fs), so this represents a sound velocity of $c_s = 3.5 \times 10^4 \text{ms}^{-1}$. The pulse was generated by reducing the lengths of the two bonds at one end of the chain by 0.05Å and allowing the chain to move without applying any damping. The over-prediction of force constants that is characteristic of CNDO is responsible for the speed obtained being rather higher than the SSH result.

Fig. 6.22 repeats the calculations of Su and Schrieffer for an end-injected soliton using the CNDO model. The dimerisation pattern is plotted at three different times; observe not only that the relaxation of the defect into a soliton appears to be occurring fairly quickly, but also that the speed at which the soliton moves up the chain remains constant to a good approximation. This velocity is 0.10 carbon atoms per time step, corresponding to approximately $1.2 \times 10^4 \text{ms}^{-1}$, a figure which is comparable to the speed of sound.

6.8 SOLITON MOBILITY

The large size of a soliton ($l \approx 8$ carbon units) implies a very low effective mass (SSH calculated that $M_{\text{eff}} \approx 6m_e$) and hence a high mobility. This is expected to be one of the reasons that t-PA can be made in such a highly conducting form (Basescu *et al.* 1987). The method of this thesis is ideally suited to the computation of the mobility within the CNDO model; such a calculation uses both the model's dynamical nature and the facility it provides for the application of an external electric field.

Fig. 6.23 shows how the dimerisation pattern of a soliton moves along a chain under the influence of an applied field of 10^{-3} a.u., or approximately $5 \times 10^8 \text{Vm}^{-1}$. Snapshots of the soliton position are shown at intervals of 5 steps (with the time step approximately 1fs as above), and it can be seen that the soliton's velocity remains fairly constant throughout the run. This velocity is measured to be $3.9 \times 10^4 \text{ms}^{-1}$, corresponding to a mobility of $0.75 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The calculation was repeated for a field five times smaller, and a slightly larger value was obtained ($\mu = 0.79 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). This difference does not appear to be due to the effects of localisation within the chain, since the soliton velocity was observed to remain so constant, but might be due to the soliton approaching its maximum velocity. Conwell and Jeyadev (1989) have suggested that effects similar to relativistic effects might increase the soliton's effective mass, and hence decrease its mobility, at velocities similar to the maximum velocity.

Experimental evidence for the soliton mobility comes from two sources: magnetic resonance experiments (Conwell and Jeyadev 1989) and picosecond studies of photoconductivity (Sinclair *et al.* 1986). Both of these sources yield approximately $1 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the mobility, in good agreement with the results of the model used here.

The soliton velocity was also calculated with an applied field two and four times as large as that applied above. The first calculation led to an approximate doubling of the soliton velocity, but when the field was

increased to 4×10^{-3} a.u. (2×10^9 Vm⁻¹) the soliton broke up rather than move along the chain as before. It therefore appears that there is a limit on the soliton velocity of something in the region of 10^5 ms⁻¹, i.e. a few times the speed of sound in t-PA. Bishop *et al.* (1984) first remarked that there should be a limit to the soliton velocity, and Guinea (1984) predicted, using a modified SSH model, that this velocity would be 4.8×10^4 ms⁻¹, larger by a factor of 2.6 than his value for the speed of sound. Such an effect clearly carries over into the CNDO calculations.

6.9 BREATHERS IN POLYACETYLENE

It was first remarked by Bishop *et al.* (1984) that the energy of photoexcitation of t-PA, within the SSH model, was greater than the energy associated with the defects assumed to be created. Photoexcitation at the band gap, with energy 1.4 eV, was shown (Ball *et al.* 1983) to lead to the formation of a pair of solitons whose energy when static was 0.45 eV each, and whose maximum kinetic energy was $\frac{1}{2} M_s v_{\text{sol}}^2 \approx 0.14$ eV each. This left an amount 0.22 eV unaccounted for, and Bishop, from numerical calculations within the SSH model, postulated that this energy could be associated with a localised vibrational defect, rather than be converted directly into phonon modes. Although the consideration of Coulomb energy within the Hubbard model appears at first sight to account for this excess energy (it was estimated in §3.6 that the energy of a charged soliton was raised by 0.11 eV from the simple SSH value), the Coulomb interaction between the two (oppositely charged) solitons introduces another term, and it is clear that the photoexcitation process needs investigation.

Calculations within an extended Huckel-type model by Wang and Martino (1986) also predicted the existence of such a localised state, as did the fact that both sets of authors were able to explain how the presence of such an excitation, known as a *breather* (or, for a time, a *bion*) could account for the hitherto unexplained photoinduced absorption peak observed

at 1.35eV, i.e. just below the band edge, in t-PA.

Wang and Martino found no fewer than three possible types of breather, each of which could be formed if the excess energy was appropriate. The lowest energy form, known as an *exciton breather*, had a distortion pattern resembling that of a polaron, but oscillating with time; the two higher energy forms were both entitled *central breathers*, and the transition between these two forms did not occur at a sharply defined energy but gradually over a range of energy. The first comprised a static soliton pair, with an oscillating distortion similar to that of a polaron superimposed, while in the second form (that of highest energy) the solitons moved up and down the chain in a periodic fashion as well. Note that within the models which go beyond SSH in their treatment of electron-electron interaction, the soliton pair is loosely bound, forming an exciton; this is also predicted by CNDO (see below), and is in agreement with the observation that the 1.35eV photoinduced absorption peak (ascribed to the breather) cannot coexist at the same temperature as photoconductivity, which occurs at higher temperatures, when the thermal energy is sufficient to break up the breather into a soliton pair (Orenstein and Baker 1982, Blanchet *et al.* 1983b).

Calculations on a molecule of t-C₄₈H₅₀, again modelling the photoexcited state by the lowest lying triplet state, support the existence of the lower energy form of central breather (fig. 6.24a-d). Because of the finite time step used, the energy in the breather is slowly dissipated in the calculation, but it is clearly seen (fig. 6.25) that the motion of the atoms within a breather is periodic, with period $\tau \approx 12\text{fs}$, corresponding to a frequency of approximately 2800cm^{-1} , very similar to the frequency of the Raman-active LO mode (§6.6), to which the breather is strongly coupled; Bishop *et al.* also found that the breather frequency was very similar to the Raman frequency.

Note that the breather is unique to t-PA; similar calculations on c-PA show

that the energy released on photoexcitation is very quickly taken up by the vibrational modes of the chain as a whole, and not localised as in t-PA. Although the behaviour of the dimerisation pattern on excitation resembles that of t-PA for short times (fig. 6.26), it soon takes the form of a defect pattern characteristic of an exciton, with an LO vibration of the whole chain superimposed (fig. 6.27). The change from localised to global vibration appears to occur within 5-10fs, and can equally be seen by examining how the dimerisation at two points on the chain varies with time (fig. 6.28). The dimerisation near the end of the chain, which remained constant in t-PA, soon begins to oscillate in unison with that at the centre of the defect; recall that the LO mode corresponds to uniform oscillation throughout the chain.

Previous authors have not studied the question of breathers in c-PA, but the absence of a photoinduced absorption peak just below the band edge in c-PA, together with the evidence that the equivalent peak in t-PA is due to a breather, provides strong evidence in support of these calculations. The possibility that the absence of a breather in the second calculation was some sort of artefact due to the shorter chain length used can be ruled out; the calculations on t-PA were repeated on a still shorter chain ($C_{24}H_{26}$) and the breather was still observed.

6.10 OPTICAL ABSORPTION AND CHARGE CONJUGATION SYMMETRY

One of the principal reasons for using the CNDO method was the desire to obtain wave functions sufficiently realistic to account for the anomaly between the experimental photoinduced absorption spectrum of PT and that predicted by Fesser *et al.* (1983) (FBC), and in §2.5 of this thesis, using the SSH model in its continuum and discrete forms respectively. The peaks observed within the band gap have been ascribed to either bipolarons or excitons, but the ratio of the intensities of the two transitions involving localised states is much smaller than that predicted by the SSH model. It

is known (Sum *et al.* 1988) that this is a consequence of the charge conjugation symmetry exhibited by that model.

GROUND STATE ABSORPTION. First, the ground state absorption pattern of t-PA was examined. The simplest method of treating the excited states, the virtual orbital (VO) method (Sadlej 1985, §8.4), was used; while a configuration interaction method might be expected to give better results, the necessary extra cost in terms of computer time and effort would be quite significant.

Although the SSH assumption that the entire π and π^* bands lie in between the σ and σ^* bands is not supported (see below), any interesting features of the absorption will be due to transitions involving either localised states within the band gap or the states at the edges of the valence and conduction bands; these are exclusively π and π^* states, so it is reasonable to ignore $\sigma \rightarrow \sigma^*$ transitions. Only matrix elements corresponding to an electric field along the axis of the chain have been considered, so there are no $\sigma \rightarrow \pi^*$ transitions.

The absorption of a $C_{24}H_{26}$ molecule, representing t-PA, near the band gap is shown in fig. 6.29; it is immediately clear that most of the absorption is due to four distinct transitions. These are $\pi \rightarrow \pi^*$ transitions, as assumed in the SSH model, and it is instructive to examine the transition weights of each individual transition. The weights of the transitions from the four highest energy valence band states to the conduction band states of $C_{24}H_{26}$ are shown in fig. 6.30. Note how each V.B. state is associated with a strong transition to one particular C.B. state, with the n 'th state from the top of the valence band being paired with the n 'th state from the bottom of the conduction band. For an infinite chain within the SSH model, these *diagonal* transitions are the only allowed transitions (Fesser *et al.* 1983).

Chain lengths in t-PA are typically rather larger than the 24 carbon atoms used as a model for the last calculation; this will act to smooth out the

apparent structure that is created by the use of a short chain as a model molecule. Furthermore, a real sample will contain chains with a range of lengths, which again will help to smooth out the apparent structure and leave a smooth interband absorption pattern. Any peaks which are due to localised states will not, of course, be smoothed out by these effects.

GROUND STATE EIGENFUNCTIONS. By looking at the eigenfunctions of the $C_{24}H_{26}$ molecule (fig. 6.31), it can be seen that these eigenfunction pairs are approximately related by CCS, but this is in fact not a meaningful test of the symmetry; it is possible for the eigenfunctions to exist in charge conjugate pairs even though CCS has been broken. It is easy to see that the inclusion of a constant second nearest neighbour hopping integral into the SSH Hamiltonian breaks CCS (Danielsen and Ball 1985) and introduces an energy shift but does not affect the eigenstates; what is less obvious is that, as long as the Hamiltonian used to represent polyacetylene (and this argument applies to both isomers) is realistic, the eigenstates *must* occur in charge conjugate pairs. It can be shown without too much difficulty that this result depends only on the terms in the Hamiltonian coupling n 'th nearest neighbour carbon atoms being independent of position for n even and alternating down the chain for n odd, both of which must automatically hold in any reasonable model for polyacetylene. In order to test CCS, we need to look at the defect states.

SOLITON ABSORPTION. The absorption pattern due to a charged soliton shows clearly the peak observed within the band gap (fig. 6.32); the peak is dominated by the transition from the state at the top of the valence band. Note that the interband transition is no longer dominated by the diagonal transitions observed for a defect-free chain; for the special case of an odd chain, it can be shown that the boundary conditions lead to wave functions which are such that the diagonal transitions are *forbidden* (Fesser *et al.* 1983), and thus many more matrix elements contribute to the interband absorption, which is therefore much smoother than for the perfect

even chain.

Since there is only one localised state associated with a soliton, CCS predicts that it must have zero amplitude at each alternate site (see §3.6). It is interesting to note that this feature does occur within the CNDO model as well, to quite a good approximation (see fig. 6.33).

BIPOLARON ABSORPTION. For some reason, the photoinduced absorption spectrum of c-PA has not been studied experimentally in the same detail as that of PT (Vardeny *et al.* 1986), but both are considered here. Both excitons and negative bipolarons are considered, and the results obtained are in excellent agreement with experiment. It was felt important to consider both polymers, since any treatment of the p_z orbitals on the sulphur atoms of polythiophene will break CCS, while the CCS-breaking terms in c-PA are much less obvious, and indeed much smaller.

The absorption pattern of a negative bipolaron in c-PA is shown in fig. 6.34; immediately it is clear that this represents a far better fit to experiment than that predicted by SSH, with two peaks of similar strength being observed. The integrated absorption intensities within each of these peaks, representing the total intensities among all the transitions from each bipolaron state in c-PA to the entire conduction band, lead to relative absorption weights of 1.5:1 for the higher state to conduction band and lower state to conduction band transitions respectively (these are the transitions labelled (1) and (2) respectively in fig. 6.34; see also the discussion of §2.5). The ratio predicted by FBC is approximately 20:1. It is seen, on examining the matrix elements for individual transitions, that the dominant terms in the absorption are the transitions between the upper bipolaron state and the lower state in the conduction band, and between the lower bipolaron state and the second term in the conduction band.

On examining the wave functions of the localised states associated with a bipolaron (fig. 6.35), it is clear that CCS is being broken at last. It

should be mentioned here that the high value predicted by the SSH model for the ratio of the strengths of the two peaks within the gap is very sensitive to the breaking of CCS; it is only necessary to change the nature of the localised wave functions slightly to obtain a very significant change in this ratio. This follows directly from the calculations of Fesser *et al.* (1983, Appendix), who showed that the precise nature assumed for the localised wave functions leads to a singularity in the calculated matrix elements.

The two absorption peaks due to transitions caused by an exciton in c-PA differ slightly in energy for up and down spins (fig. 6.36). The difference is not great, however, and the total absorption appears to contain only two peaks within the band gap. Just as was observed for the bipolaron, the two low-energy transitions are of comparable intensity; the SSH result above is independent of the occupations of the higher and lower localised states, so should be applicable to an exciton as well as to a bipolaron.

The localised wave functions due to an exciton give us a clearer picture of the precise nature of CCS. It is found that the occupied eigenstates for spin up electrons are approximately related by the usual transformation $a_{nk} \rightarrow (-1)^n a_{nk}$ to the unoccupied spin down states. For the localised states, the relationship is almost exact (fig. 6.37). Bearing in mind that the number of spin up electrons is the same as the number of spin down holes for the case under consideration, it is clear that there is a fair degree of electron-hole symmetry, and that the principal error in the SSH treatment is the attempt to use the symmetry in cases where it does not apply. Specifically, the absorption weights for spin up electrons are calculated wrongly because the spin up band itself is not charge conjugate symmetric, since it contains different numbers of electrons and holes.

Polythiophene displays very similar results to c-PA (figs. 6.38 and 6.39). The main difference is a slight change in the relative weights predicted

for the transitions involving localised states, with relative weights of about 1.5:1 being observed for the exciton as well as the bipolaron. SSH predict a slightly lower ratio than for c-PA, but still one almost an order of magnitude higher than that observed. It is gratifying to note that the experimentally observed ratio of approximately 1.5:1 (Vardeny *et al.* 1986) agrees almost precisely with that calculated here.

6.11 BETA-CAROTENE

Although β -carotene (fig. 6.40) is not strictly a conjugated polymer, the length of the central section is such that it is expected to display some properties that are characteristic of the polymers studied in this thesis. It is a molecule that is important in nature, and furthermore has the advantage over t-PA that it can be crystallised (Vaala *et al.* 1973), which would greatly facilitate the study of anisotropic effects. A few calculations have been performed here, and they support the hypothesis that β -carotene should mimic the effects seen in polymers. For speed of calculation, the methyl groups throughout the molecule were replaced by hydrogen atoms in the calculations; this seems a valid approximation to make when just beginning the study of the molecule.

The conjugation of the central section reduces the bond length alternation, just as for polymers; calculation of the structure of an exciton leads to a familiar pattern for the distortion (fig. 6.41). The dimerisation enhancement associated with the ends of a polymer chain is not seen in the ground state or the exciton, which may be due either to the presence of the rings at each end of the chain or to the single cis-type linkage.

The calculated optical absorption from the ground state (fig. 6.42) closely resembles that of $C_{24}H_{26}$ (see fig. 6.28); the absorption has been convoluted with a slightly broader Gaussian in this case, in order to improve the fit to experiment (fig. 6.43, with acknowledgements to M.J.McNamee). The spectrum agrees qualitatively with experiment in that it predicts the existence of a number of subsidiary peaks, although their

relative weights differ slightly from experiment, and it seems reasonable therefore to ascribe these experimental peaks to higher $\pi \rightarrow \pi^*$ transitions.

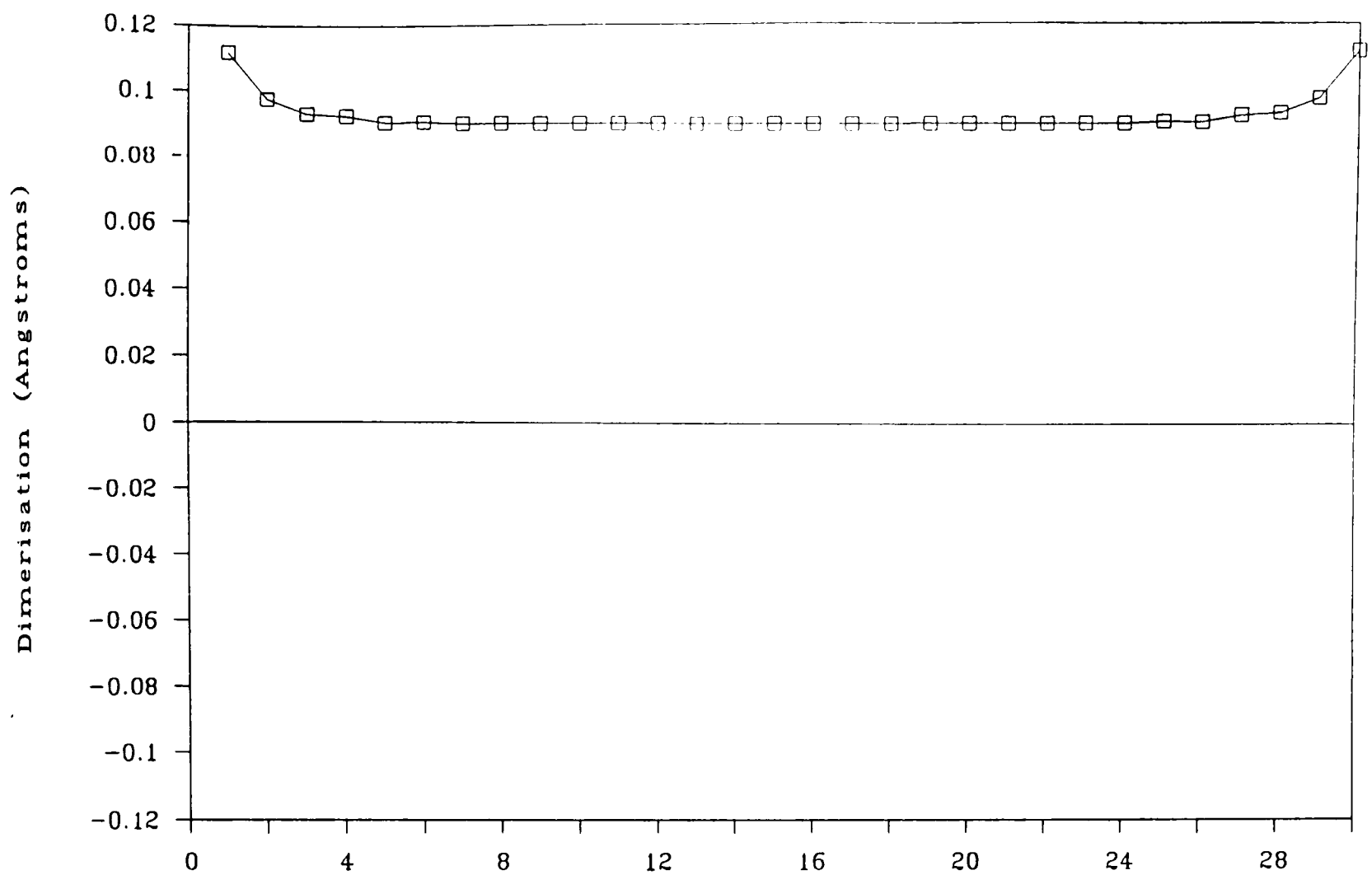


Fig. 6.1 Ground state dimerisation of c-PA. Note that the dimerisation is slightly enhanced at the ends of the chain.

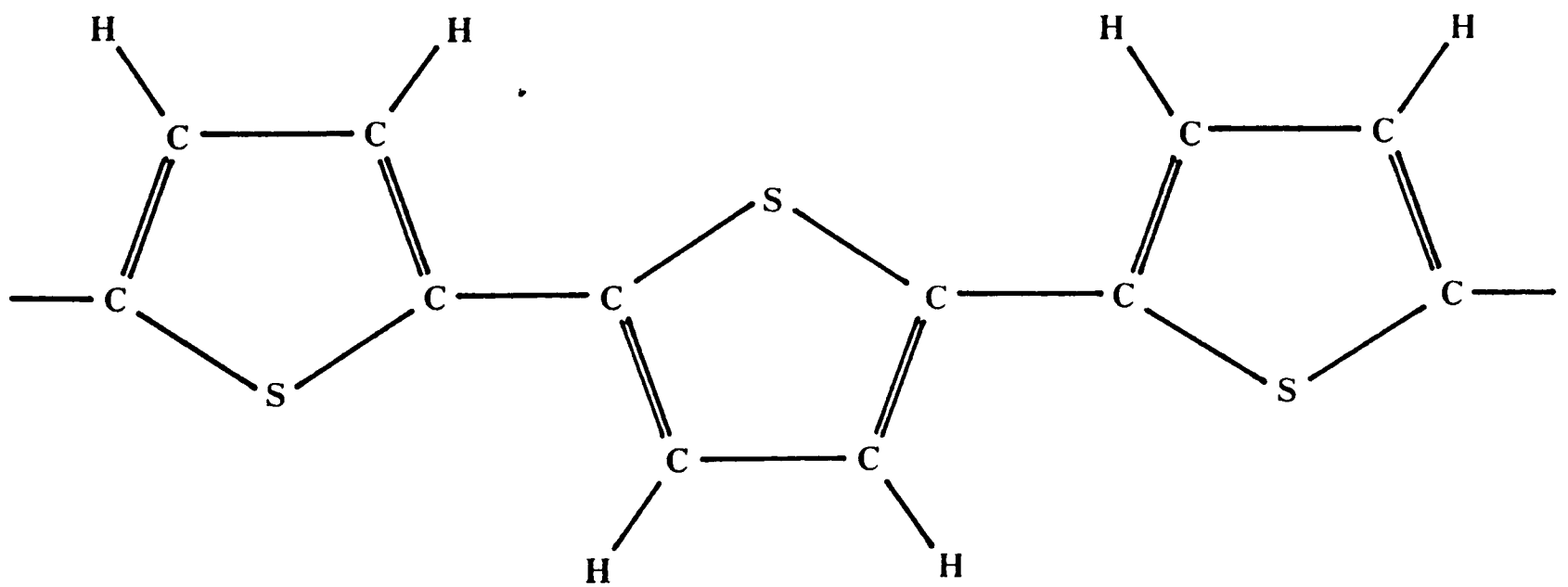


Fig. 6.2 Structure of polythiophene (PT)

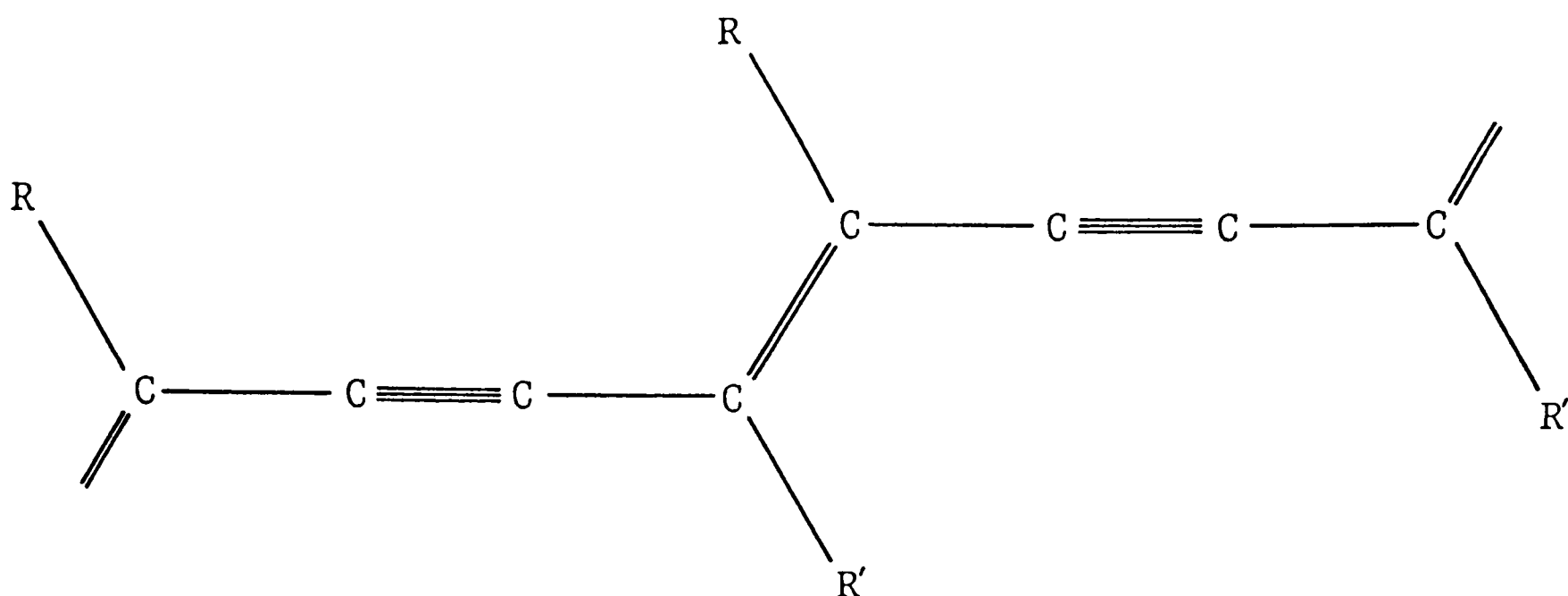


Fig. 6.3 Structure of a general polydiacetylene. There are two pairs of π electrons within the triple bonds, of which one pair lies in the plane of the molecule and only the other pair is involved in the conjugation.

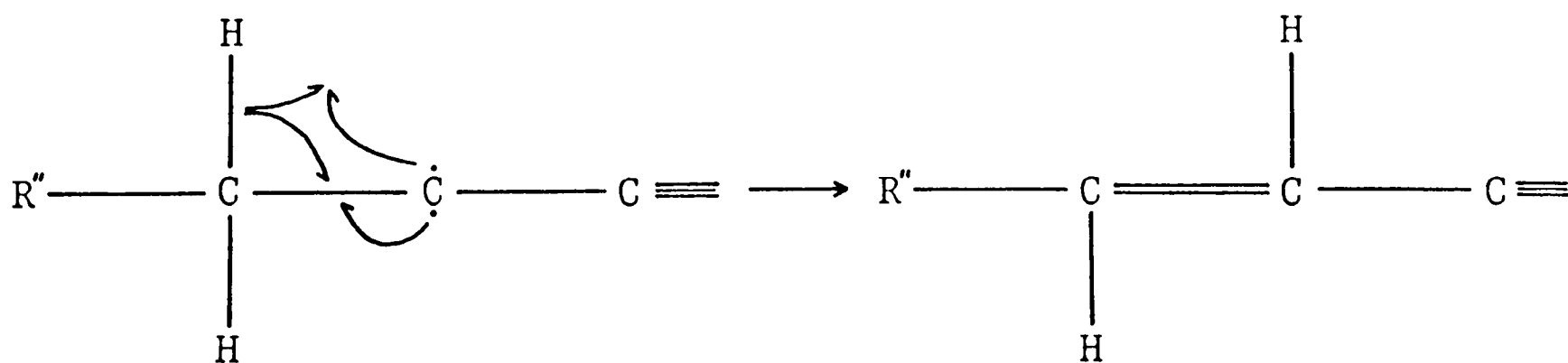


Fig. 6.4 Suggested mechanism for termination of the polymerisation of a diacetylene. Since polymerisation preserves the crystallinity of the sample, any termination mechanism must be intramolecular; the mechanism suggested here is an insertion reaction typical of carbenes.

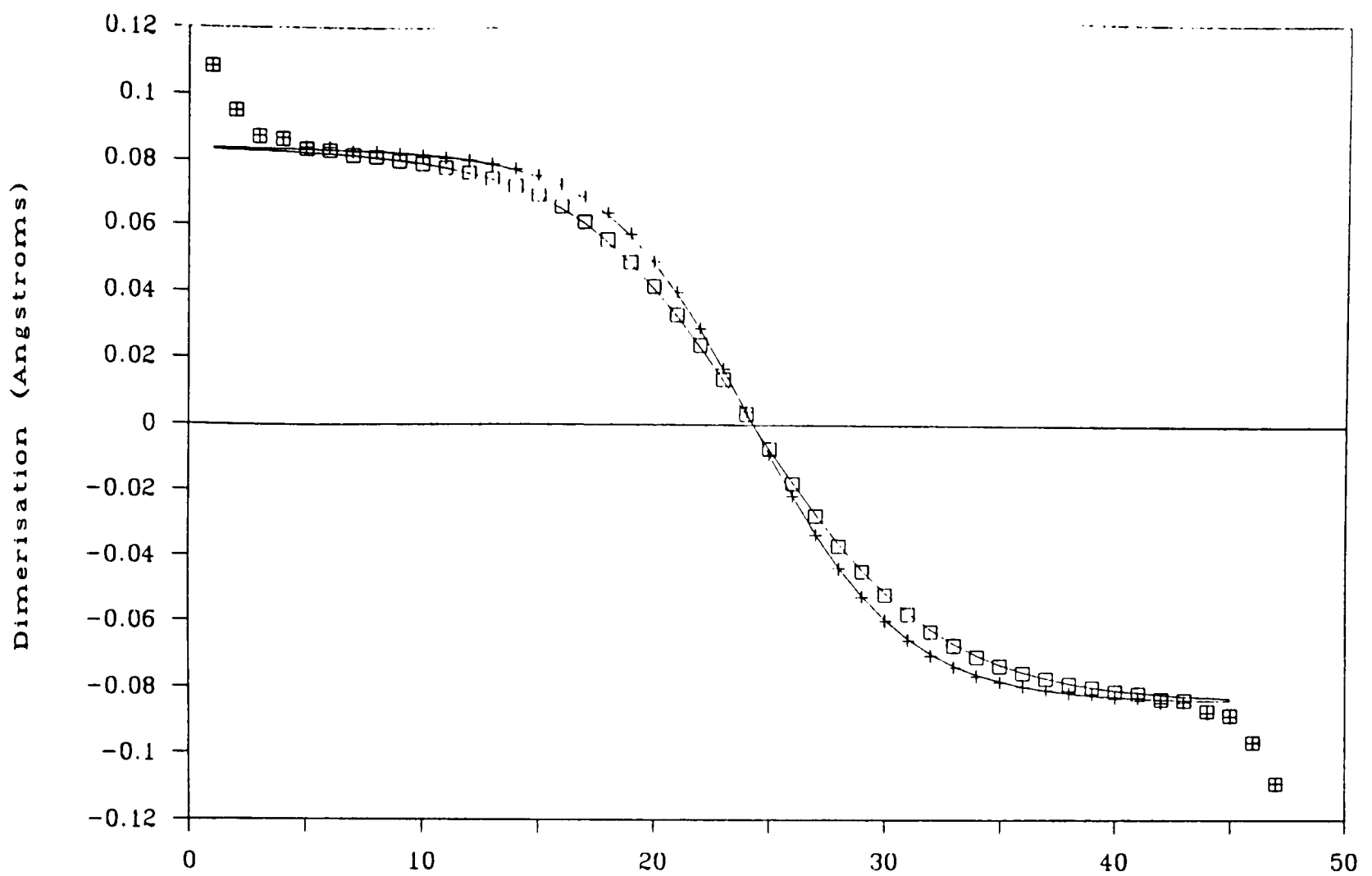


Fig. 6.5 Dimerisation patterns of charged (squares) and uncharged (crosses) solitons. The fitted curves are of the form $d_0 \tanh(x/\ell)$, with half-widths of 8.1 and 6.5 carbon atoms for the charged and uncharged solitons respectively.

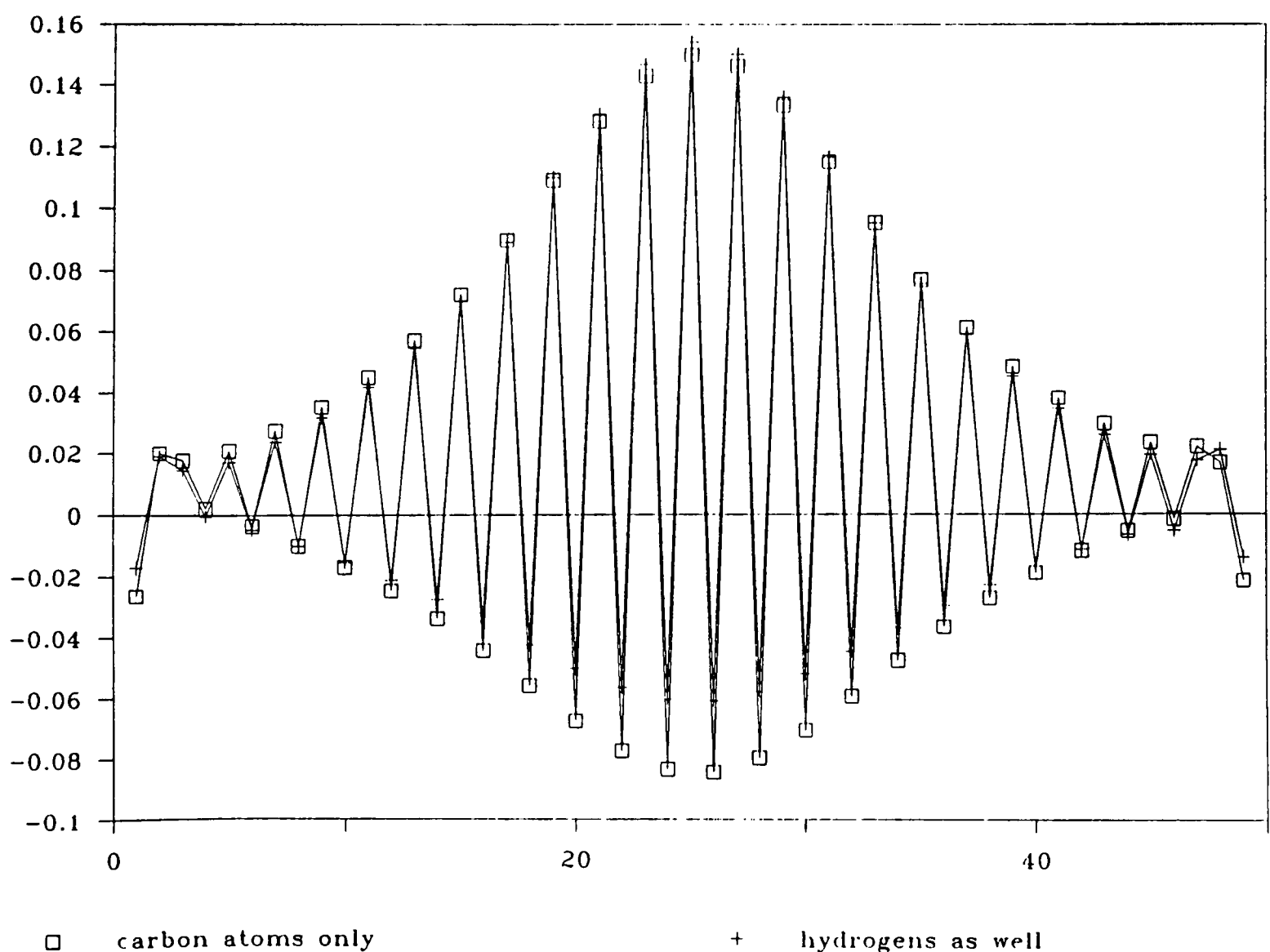


Fig. 6.6 Charge storage in a soliton. The charge is stored in such a fashion that alternate carbon atoms actually bear *opposite* charge, a counter-intuitive result that is in agreement with experiment.

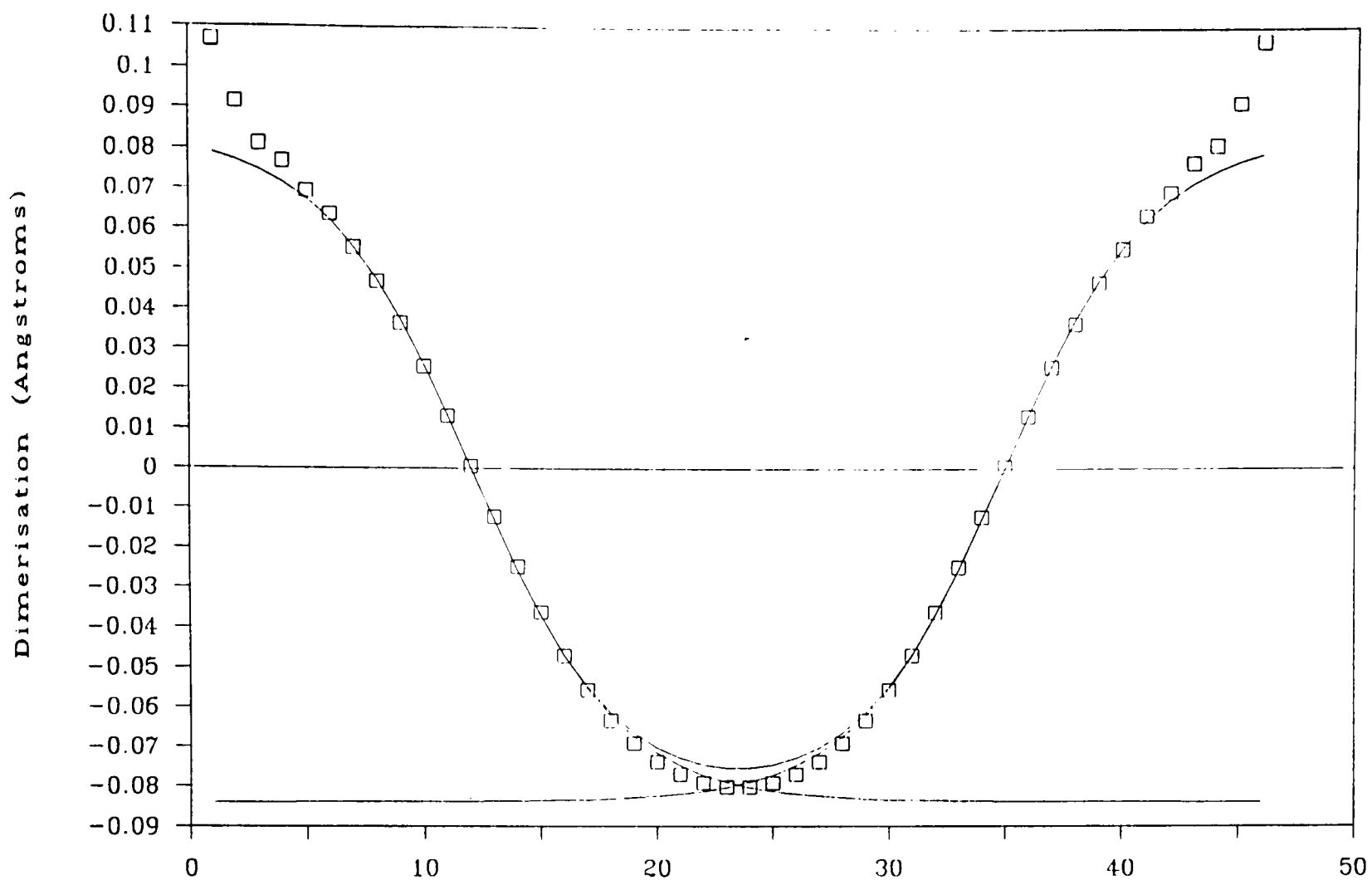


Fig. 6.7 Dimerisation pattern of a doubly charged t-PA chain. Tanh functions have been fitted to each of the resulting solitons, and the sum of the tanh functions is a good fit to the dimerisation. The distortion at the centre of the chain is actually slightly greater than that of the tanh functions, indicating how the two solitons repel each other. The distance between the solitons is, of course, limited by the chain length.

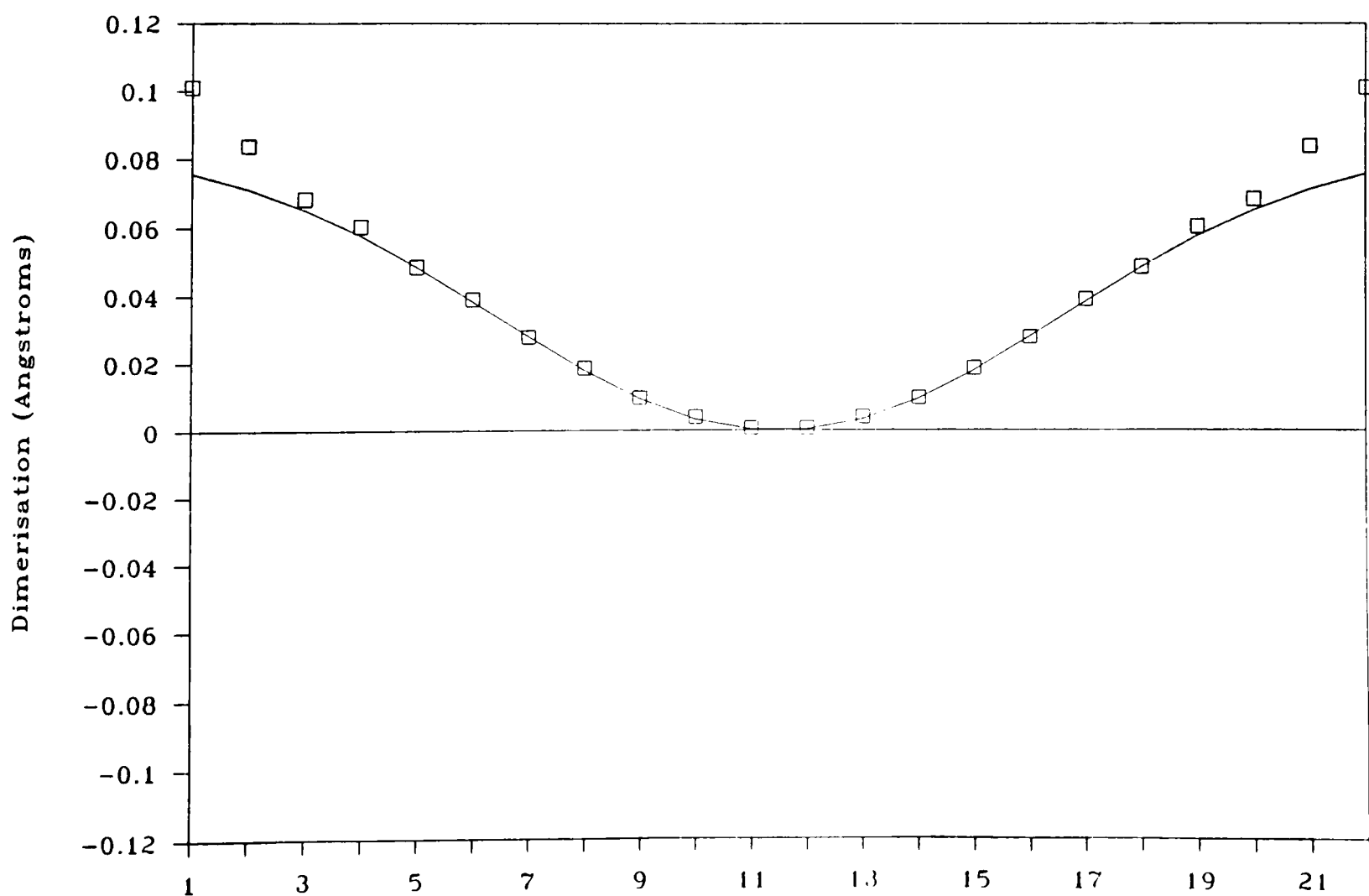


Fig. 6.8 Dimerisation pattern of a polaron in t-PA. The curve is a fit to the sum of two tanh functions, of width 5.1 and separation 9.4 carbon atoms.

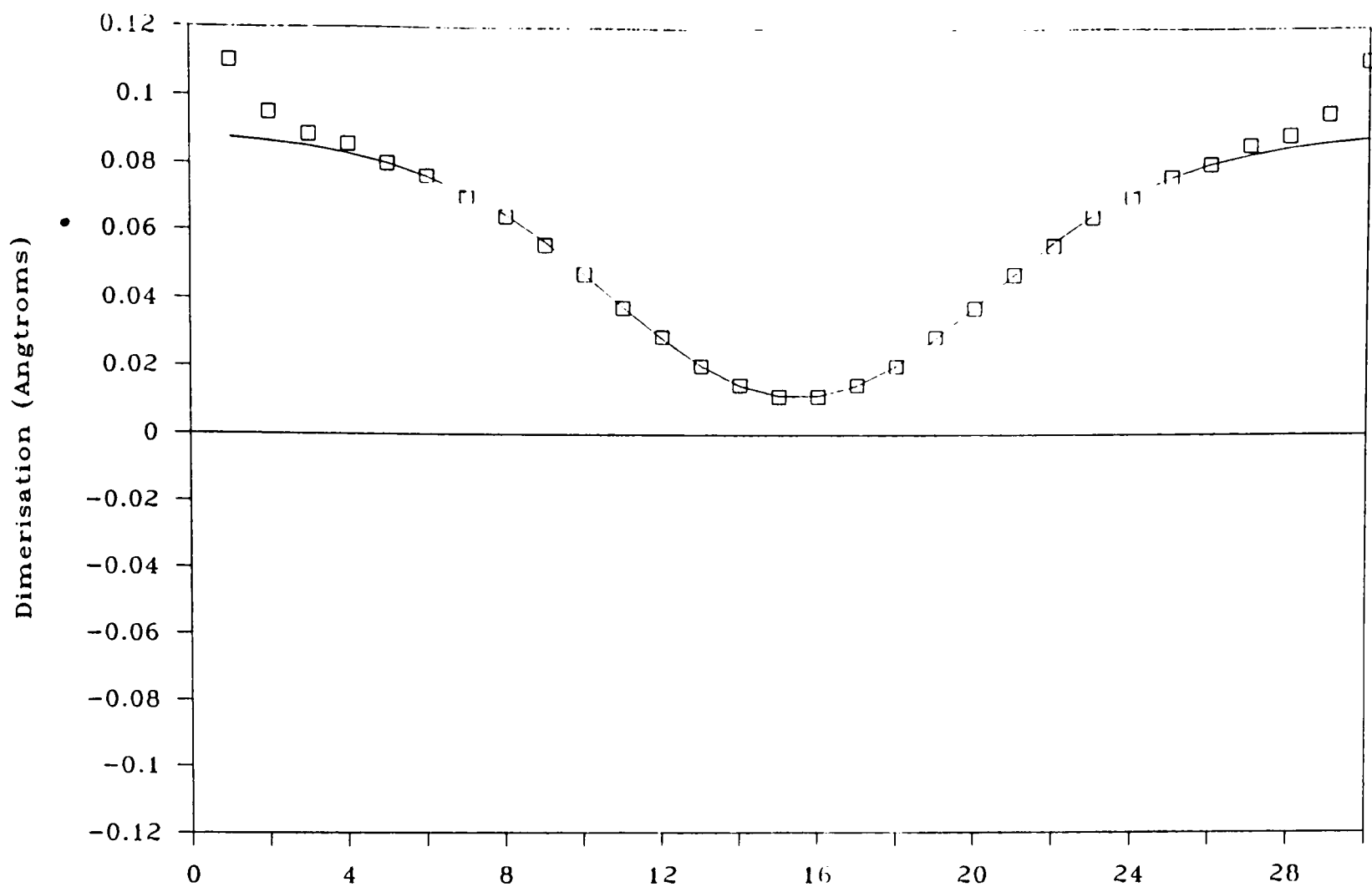


Fig. 6.9 Dimerisation pattern of a polaron in c-PA. Again, the curve is a fit to the sum of two tanh functions. In this case, the absence of ground state degeneracy means that the distortion is slightly more localised than in t-PA.

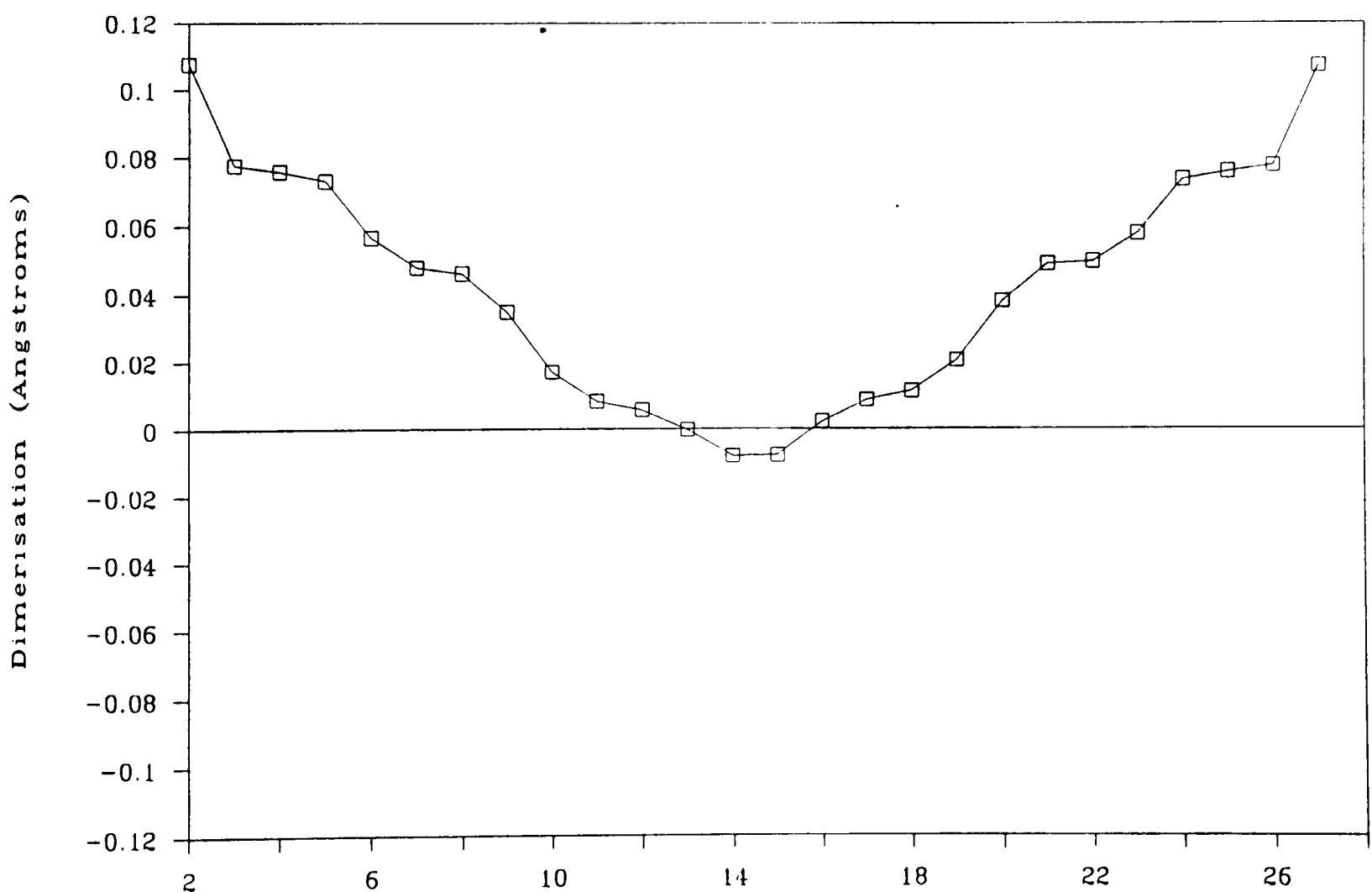


Fig. 6.10 Dimerisation pattern of a polaron in PT. Since there are now two inequivalent C-C single bonds, the dimerisation does not appear as a smooth curve, but it can still be seen that the shape loosely resembles that of the polaron in t-PA (fig. 6.8), rather than its equivalent in c-PA (fig. 6.9). This is an indication of how the degeneracy breaking is much weaker in PT than in c-PA.

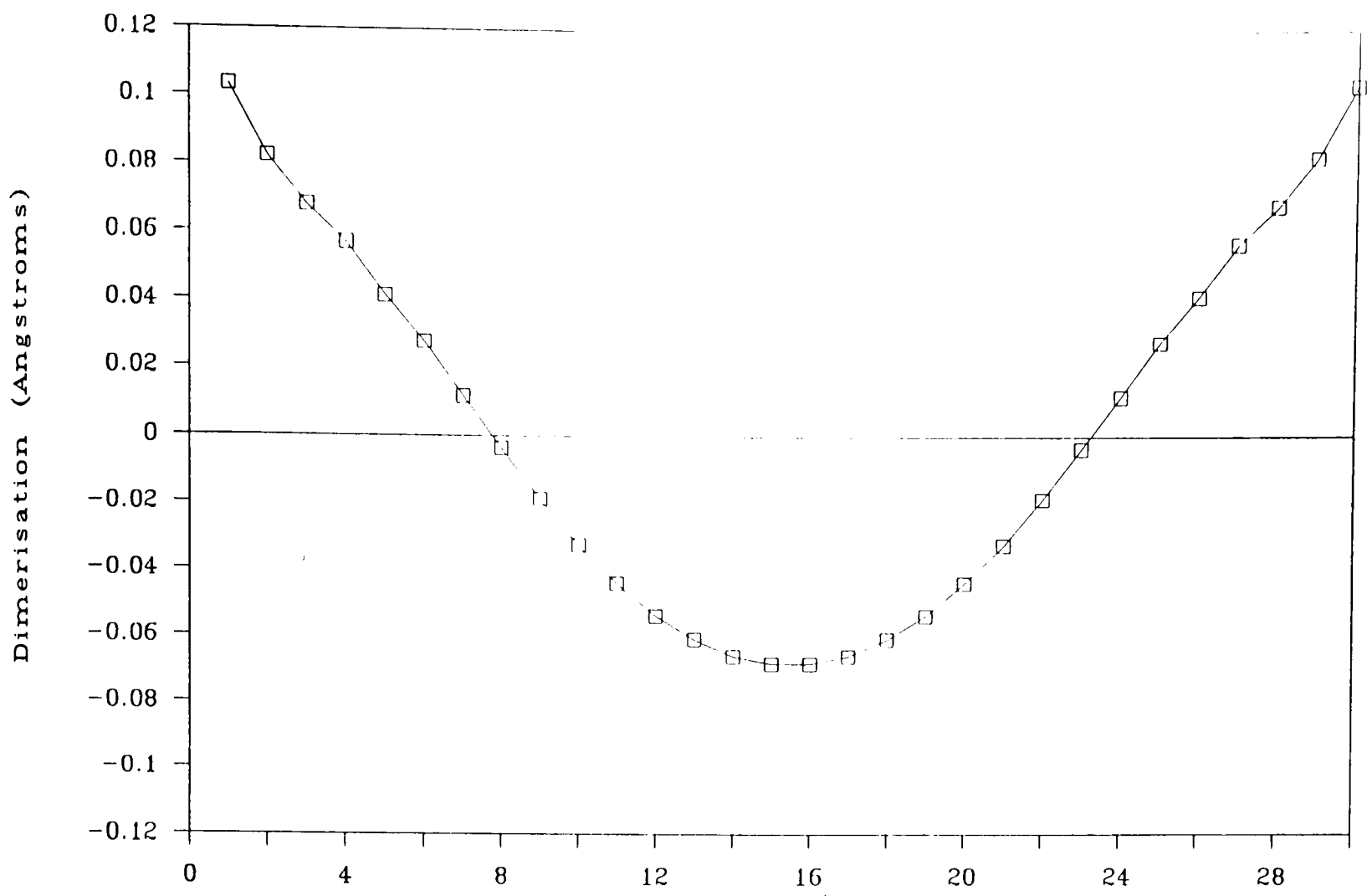


Fig. 6.11 Dimerisation pattern of a bipolaron in c-PA. The distortion predicted is significantly greater than that predicted by the SSH model (fig. 2.15).

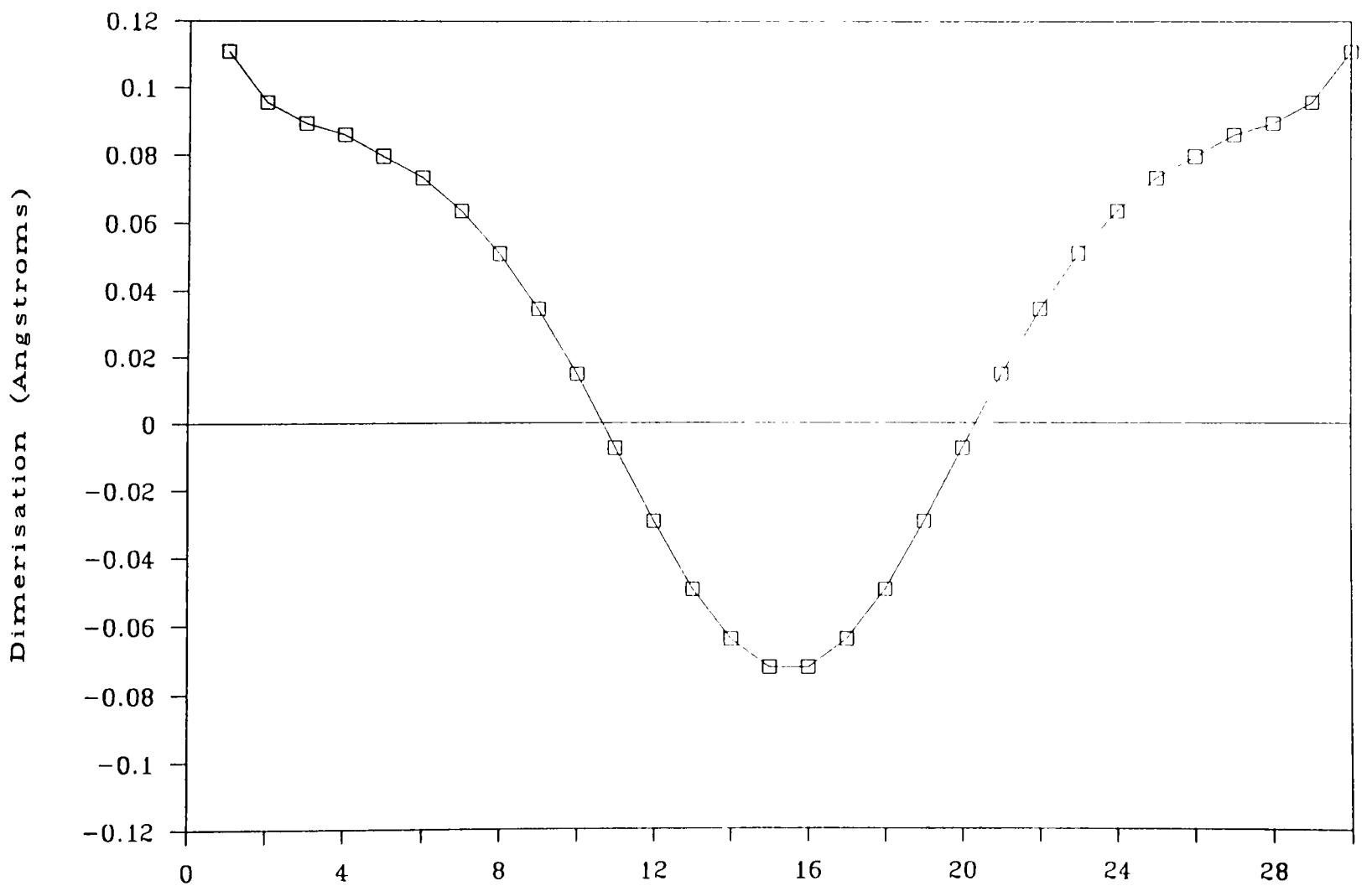


Fig. 6.12 Dimerisation pattern of an exciton in c-PA. The SSH model predicts that this figure should be identical to fig. 6.11, by charge conjugation symmetry; in fact, the lack of the Coulomb repulsion term has enabled the defect to become narrower, although its amplitude is similar to that of the bipolaron.

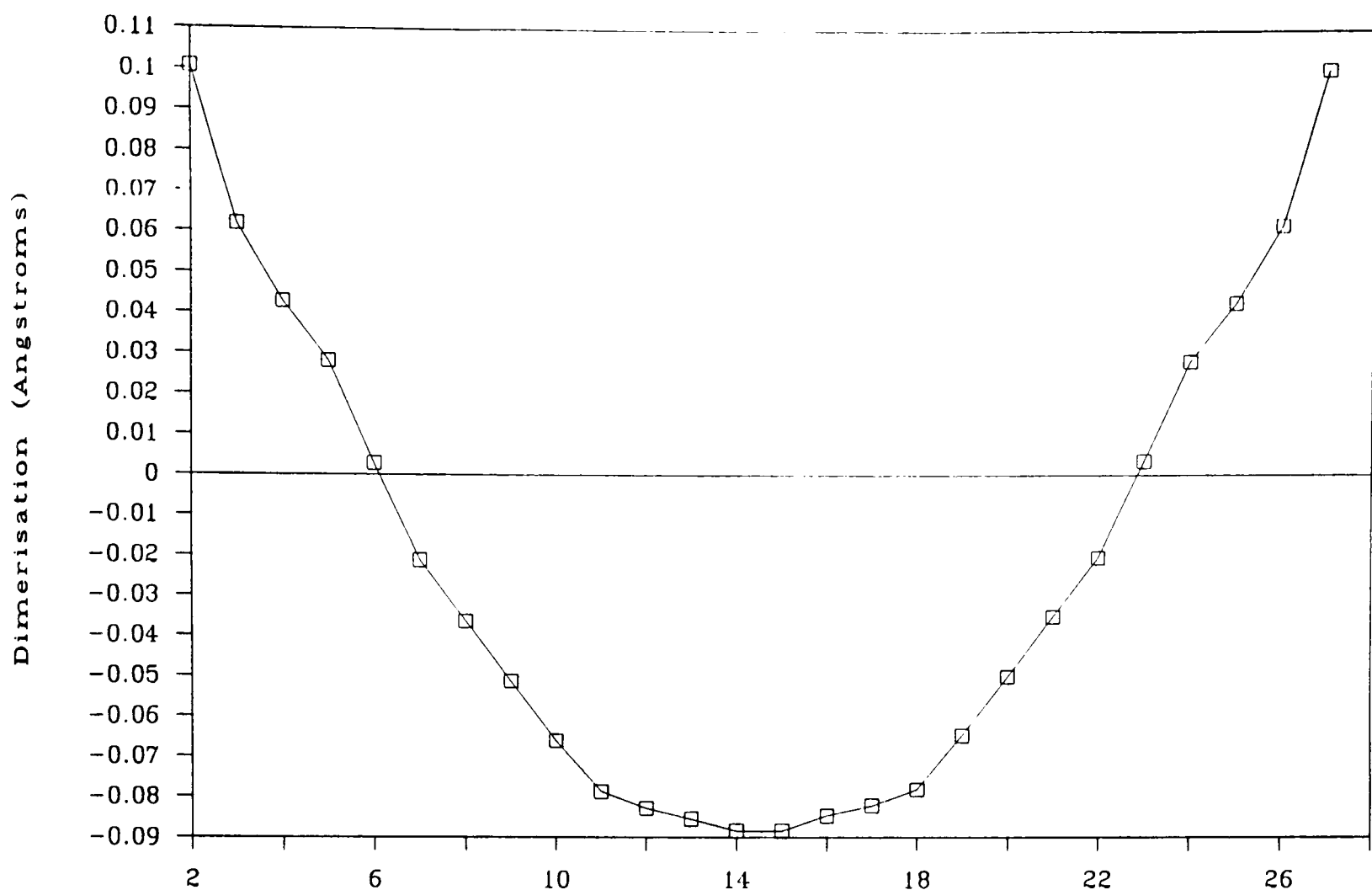


Fig. 6.13 Dimerisation pattern of a bipolaron in PT. The defect is possibly being artificially localised by the chain ends; in any case it is clear that its natural extent is much larger than that of its equivalent in c-PA, again due to the reduced strength of the degeneracy breaking.

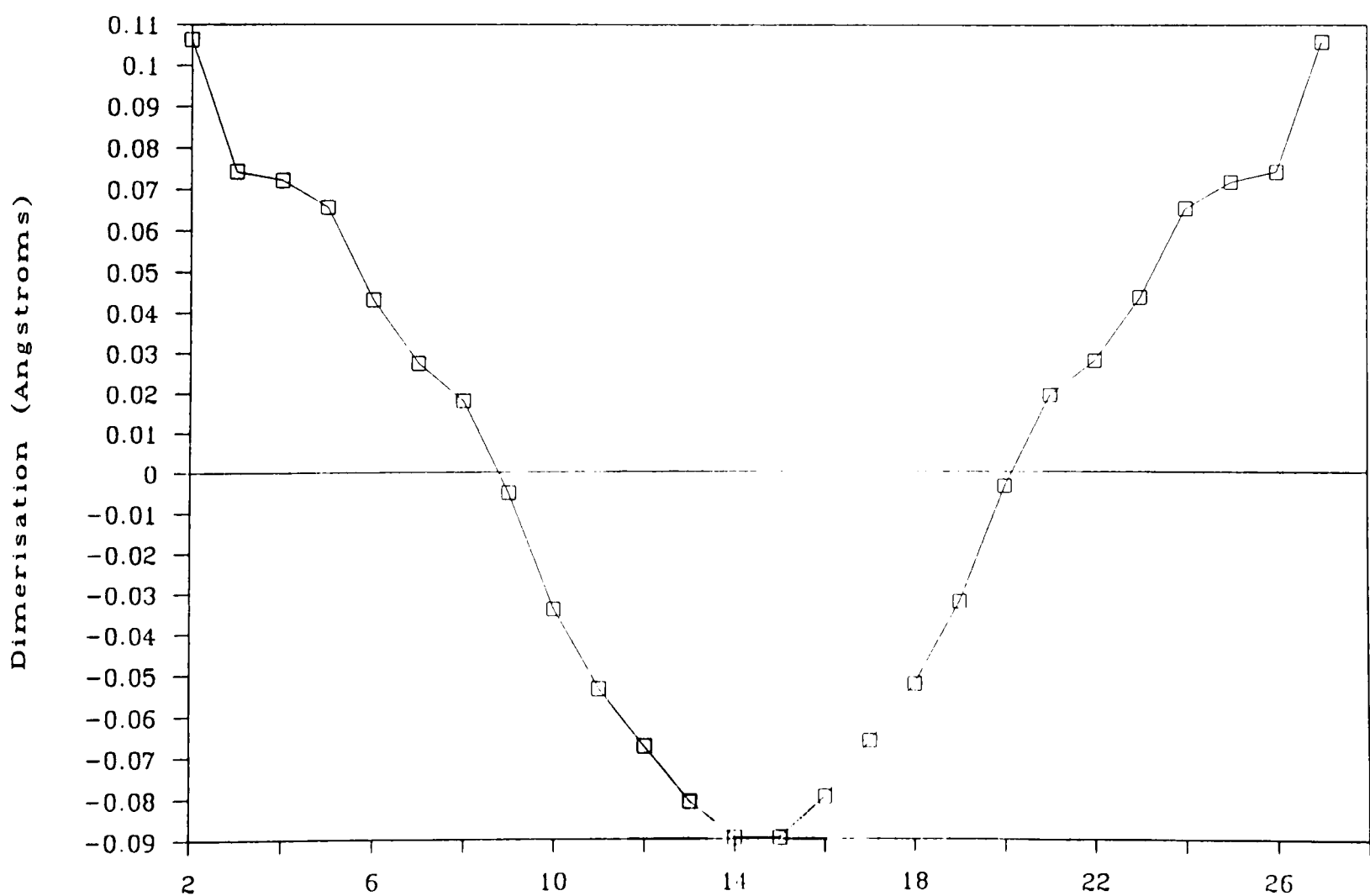


Fig. 6.14 Dimerisation pattern of an exciton in PT. Again, the defect is of similar amplitude, but smaller width, than the bipolaron.

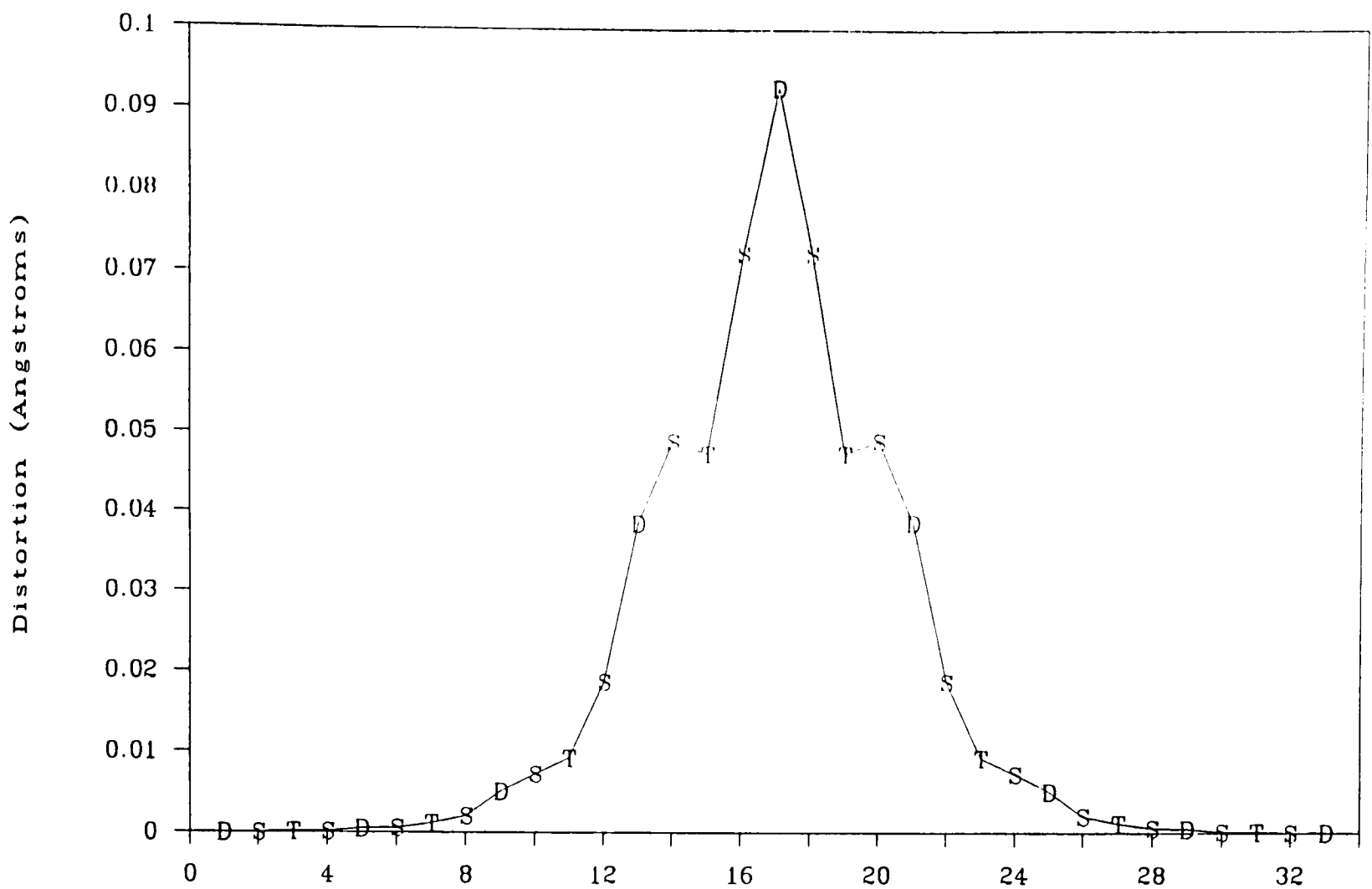


Fig. 6.15 Dimerisation pattern of an exciton in PDA, where the defect is centred at a double bond joining diacetylene monomers. The presence of triple bonds means that it is not possible to define a smoothly varying dimerisation parameter in the same way as for polyacetylene, so the quantity plotted here is the amount by which bond lengths have changed from their ground state values, with a factor $(-1)^n$ included in order to ensure that a distortion that shortens single bonds and lengthens double bonds corresponds to a positive value throughout. The values are labelled D, S and T according to whether they represent double, single or triple bonds.

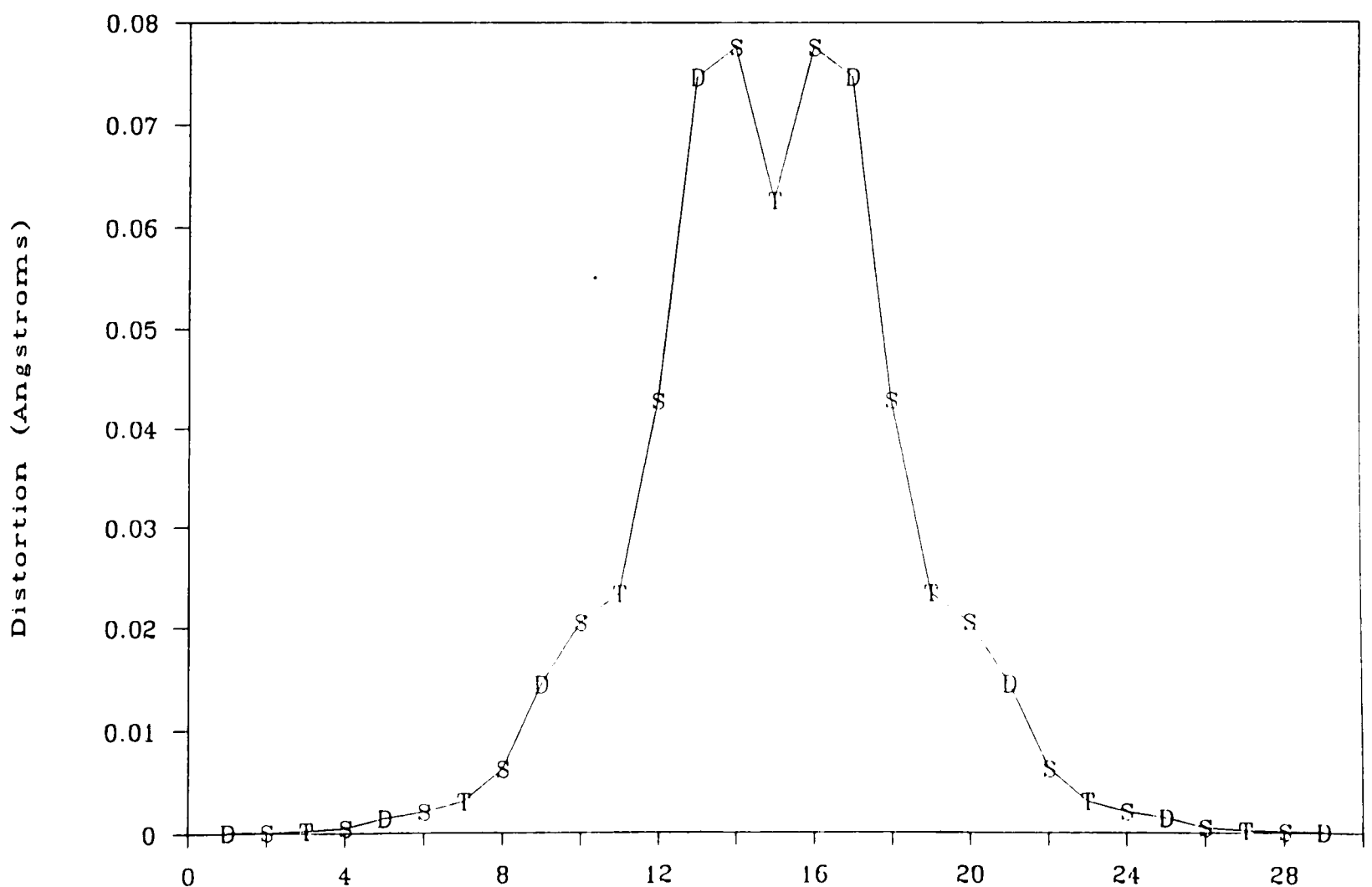


Fig. 6.16 Dimerisation pattern of an exciton in PDA, this time with the defect centred at a triple bond within a diacetylene monomer. The excitons of this figure and fig. 6.15 are virtually degenerate.

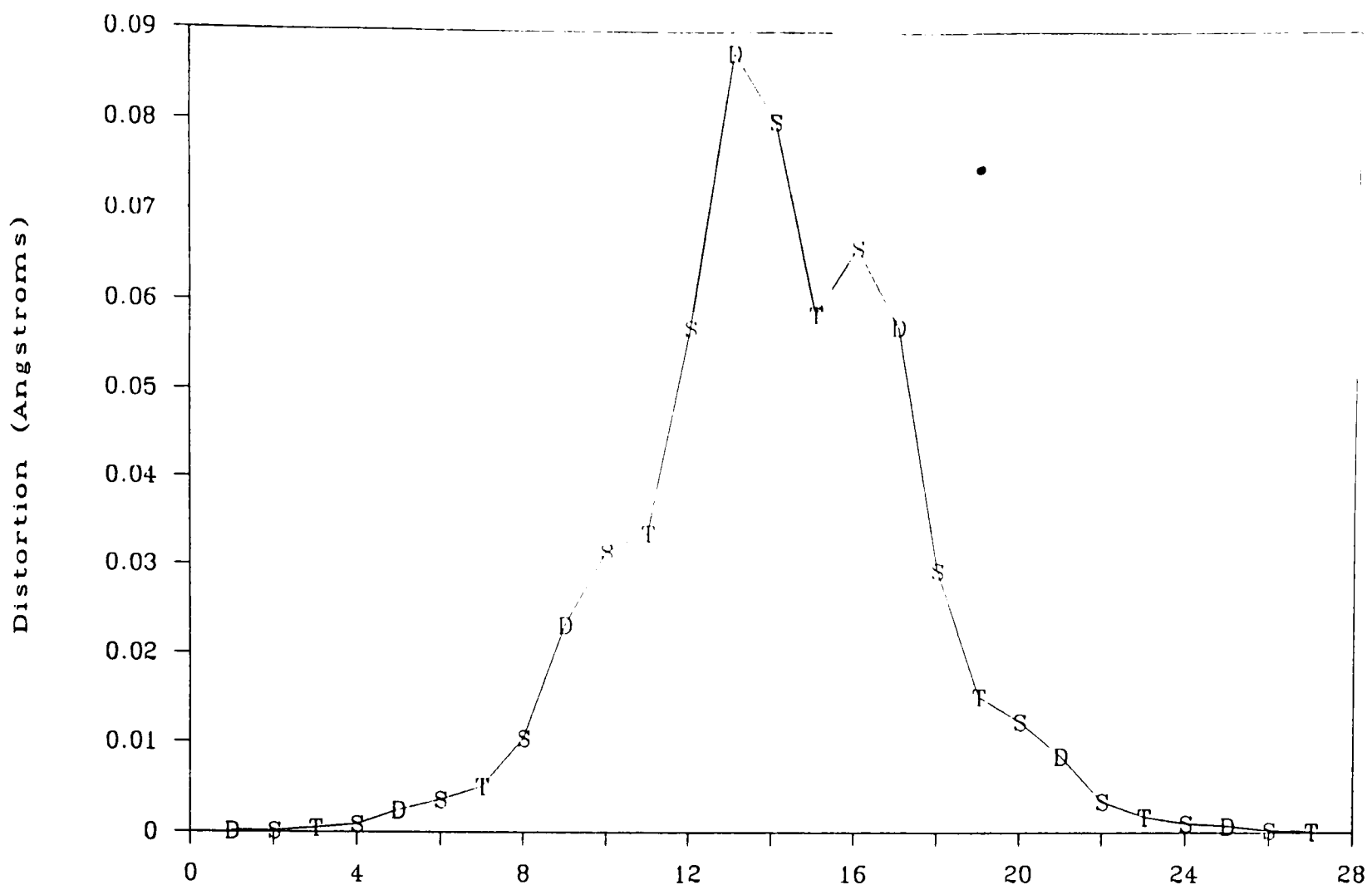


Fig. 6.17 Dimerisation pattern of an exciton in PDA, with no symmetry constraints. Although the interaction between the defect and the ends of the chain is very slight, the fact that the difference in energy between double and triple bond centred excitons is weaker still means that the exciton is pushed into the middle of the chain, rather than being centred on a multiple bond.

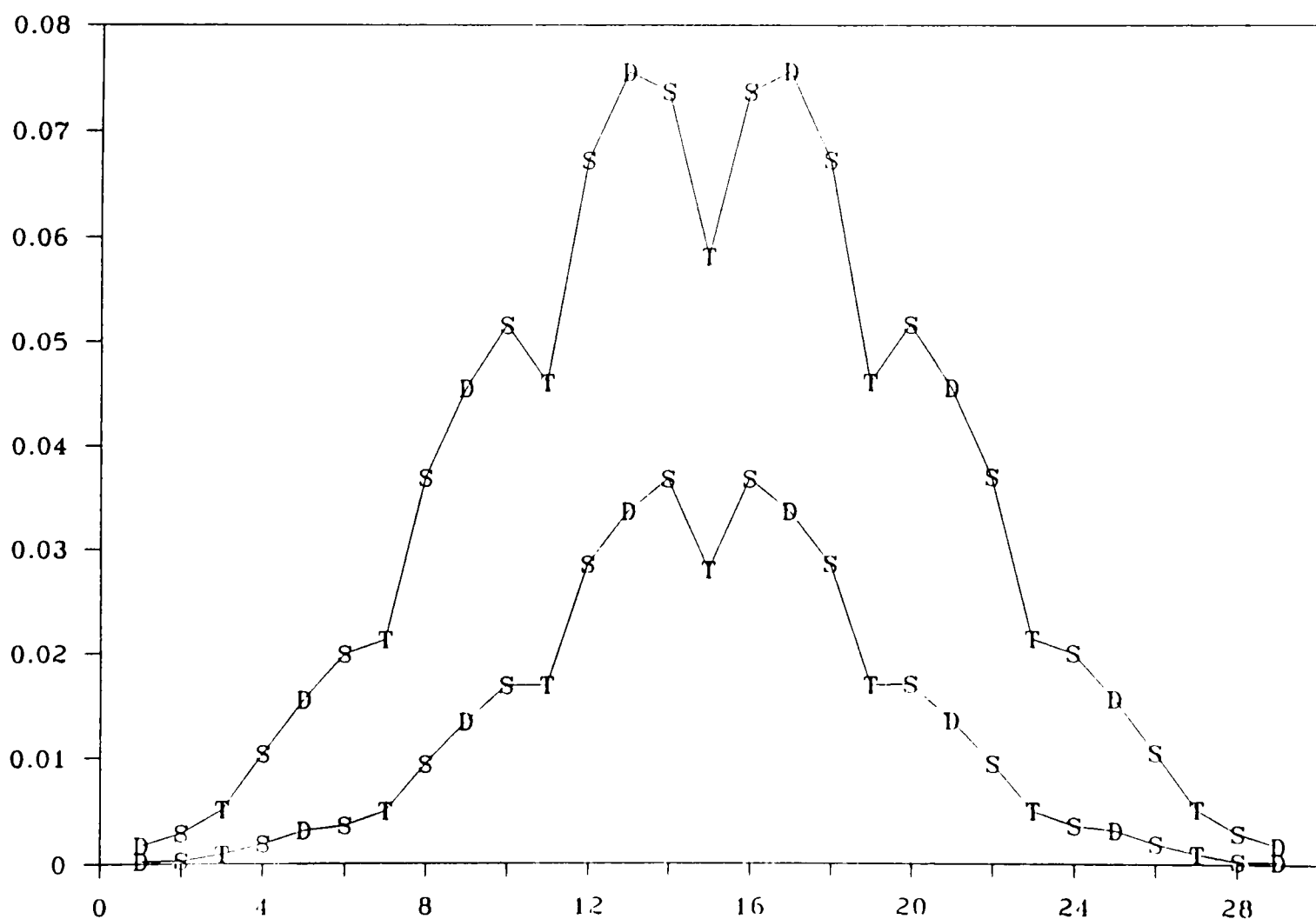


Fig. 6.18 Dimerisation patterns of a polaron (lower curve) and a bipolaron in PDA, where the defects have been centred at triple bonds. The defects resemble those of c-PA in their amplitude and extent, implying that localisation due to the non-degeneracy of the ground states is quite strong.

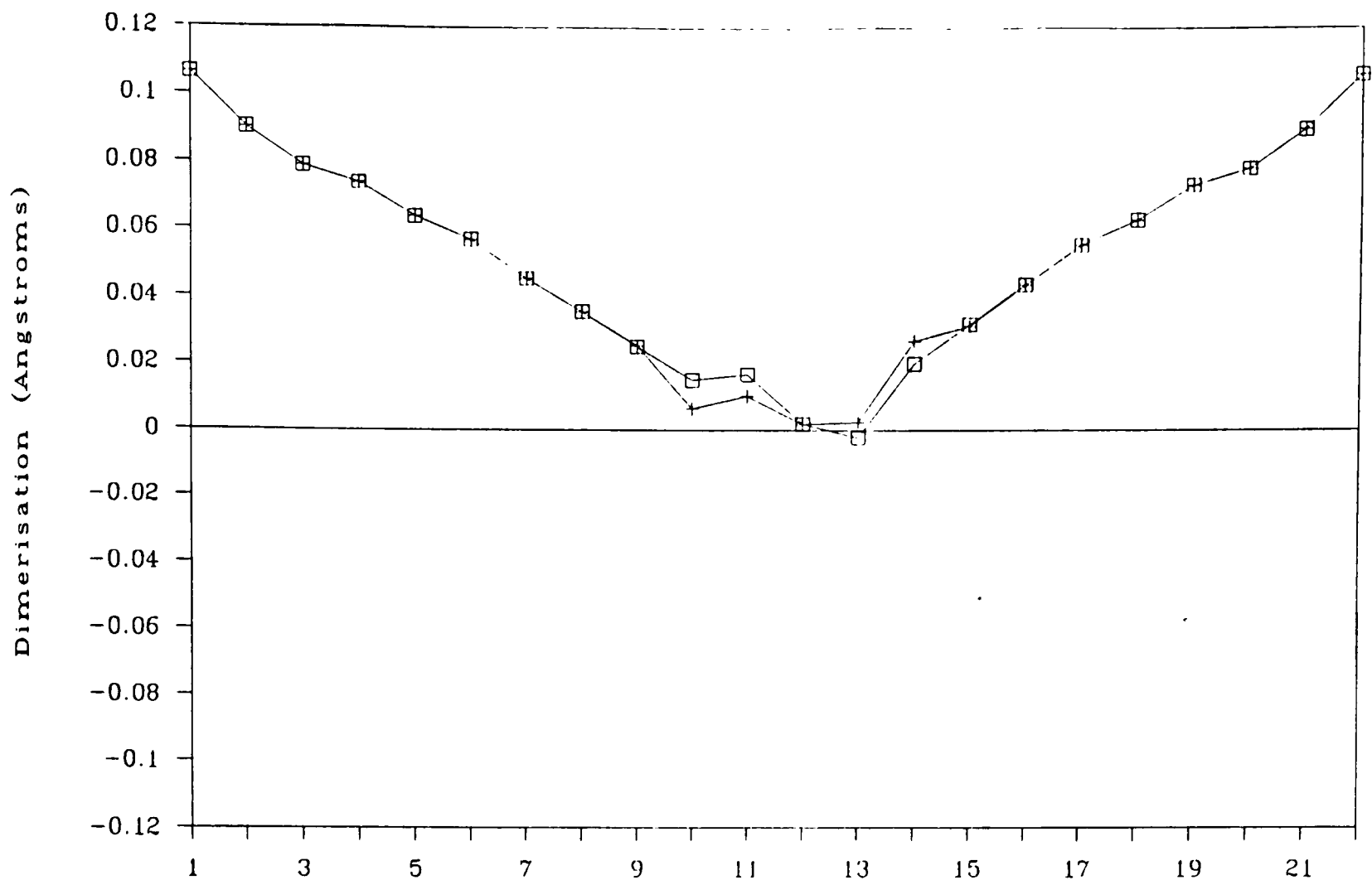


Fig. 6.19 Dimerisation pattern induced in a t-PA chain by a nearby sodium atom (which settled at about $2.5\text{\AA}$ from the chain). The crosses correspond to a dimerisation parameter calculated in terms of actual bond lengths; the squares to a dimerisation parameter which only treated the in-plane component of the atomic distortion. The overall effect is of a shallow polaron-like distortion over a range typical of defects in t-PA, with a further short-range distortion of a few bonds near the sodium atom. The apparent asymmetry of the curves is due to the system being started from an asymmetric initial state, with relaxation not being 100% complete.

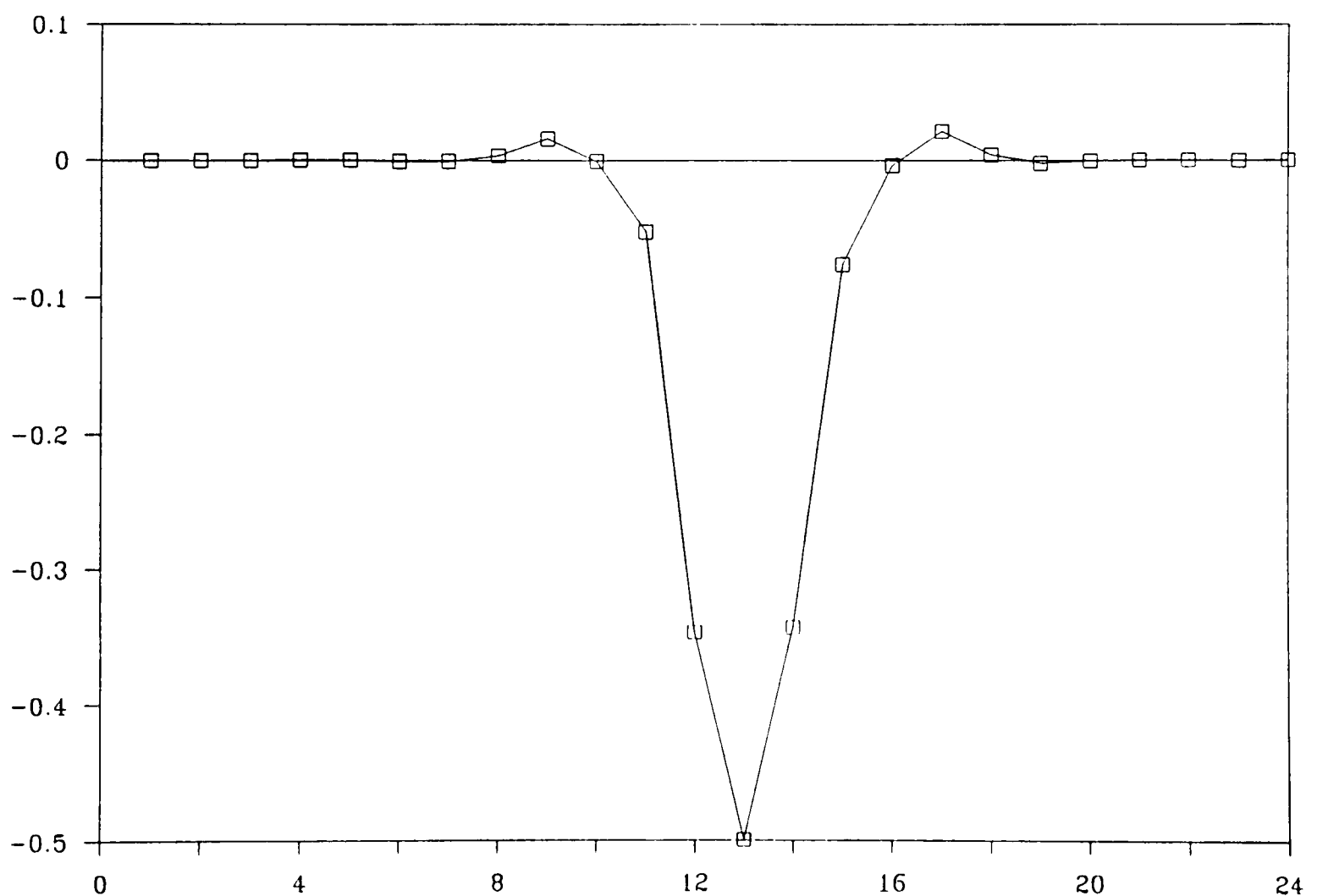


Fig. 6.20 Distortion of a t-PA chain (in atomic units; $1\text{ a.u.} \approx 0.5\text{\AA}$) out of the molecular plane, caused by doping with a sodium atom above the plane. There is a weak, long-range attraction due to Coulomb forces, and a much stronger repulsion over a shorter range.

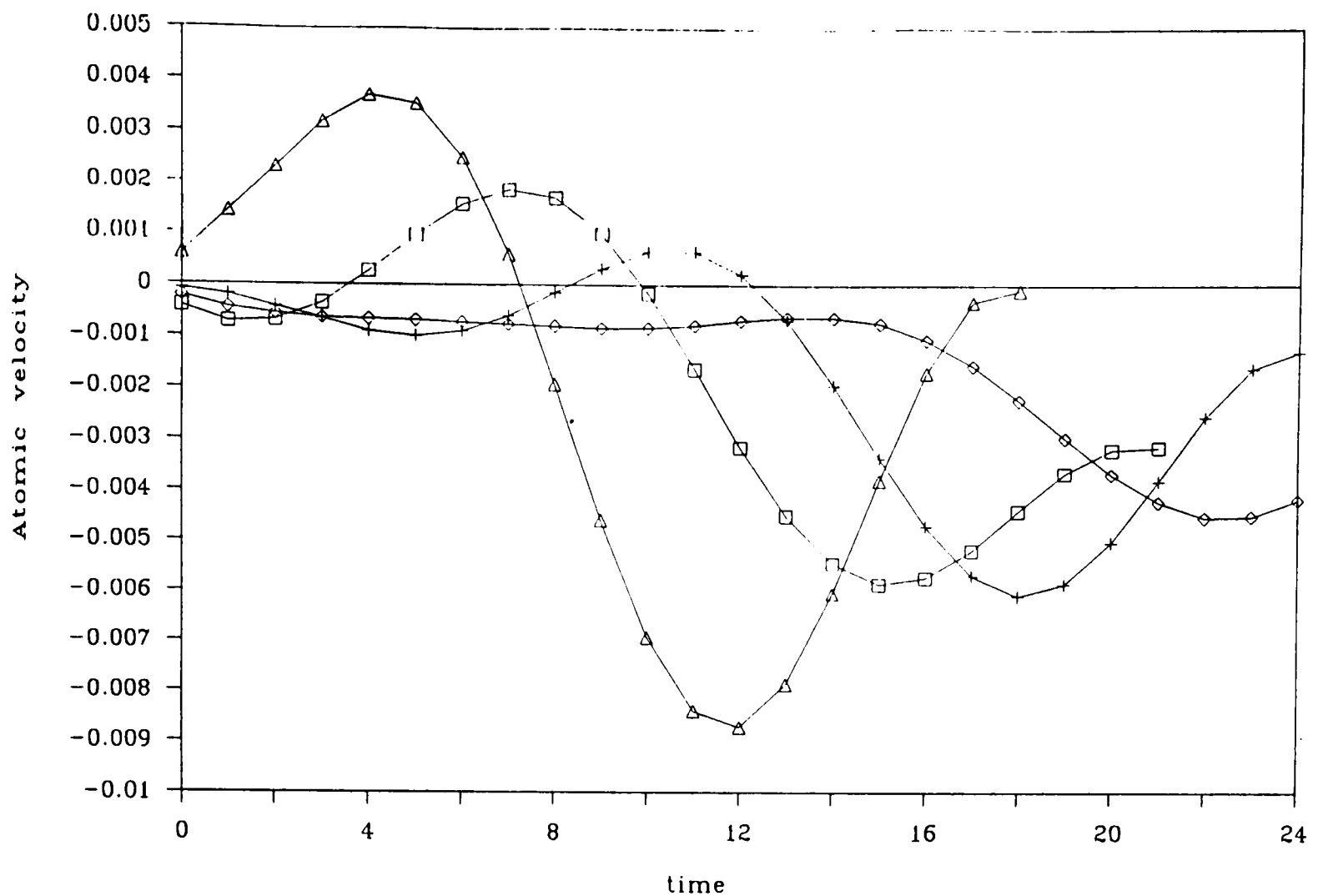


Fig. 6.21 Calculation of the speed of sound in t-PA, as measured by the speed at which a pulse travels down the chain. The chain was started at $t=0$ with the two bonds at one end of the chain artificially shortened from their ground state values, and here the resulting velocities of atoms further down the chain are plotted against time (Δ :atom 3; $\square$:atom 4; $+$:atom 5; $\diamond$:atom 6). Note that the pulse, while attenuated as it travels, does approximately keep its shape, and a velocity of $3.5 \times 10^4 \text{ms}^{-1}$ can be deduced (see §6.7).

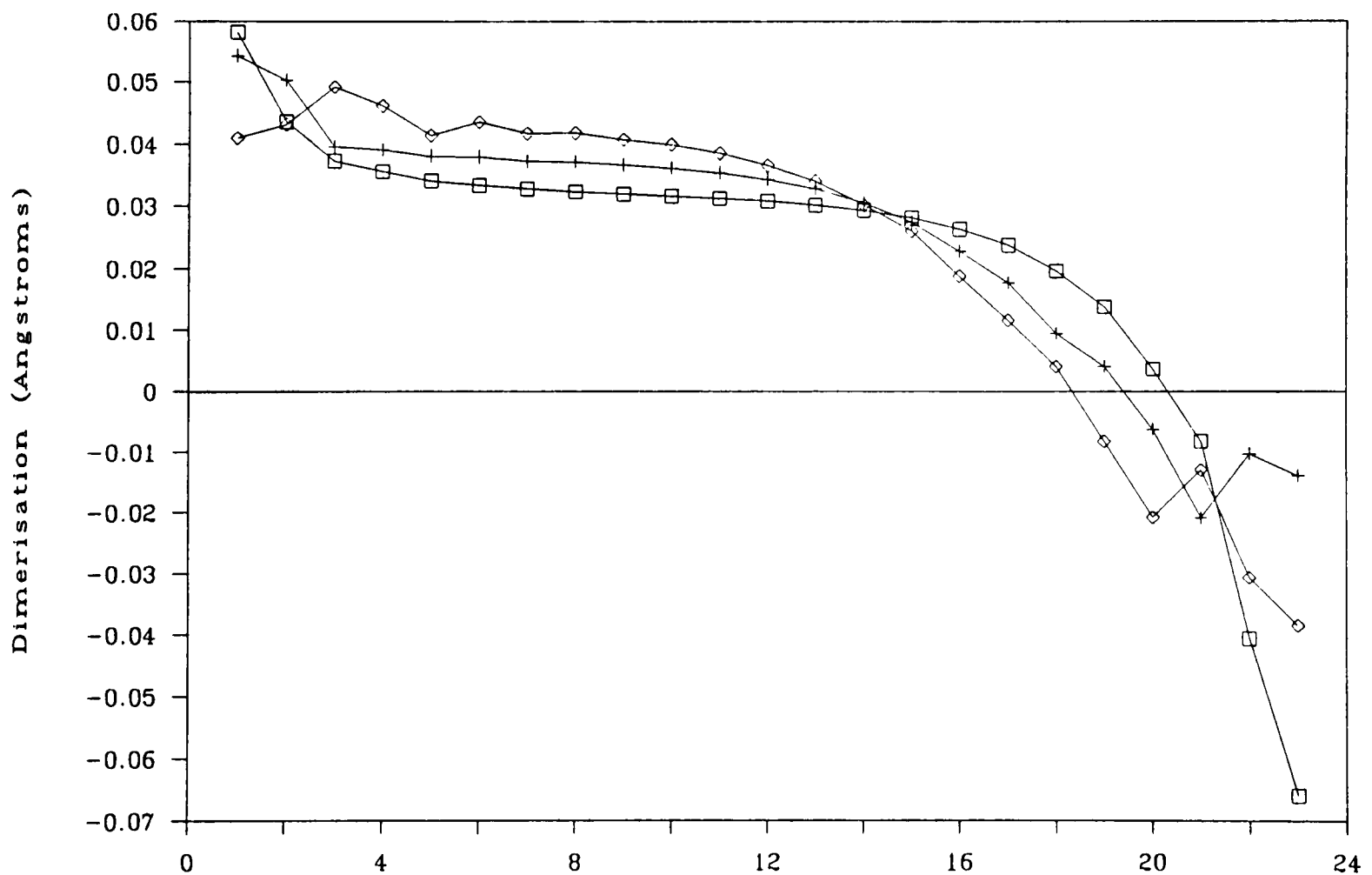


Fig. 6.22 Indication that an odd chain with uniform dimerisation will relax into a chain with a soliton (c.f. fig. 1.5). The distortion pattern approaches that of a soliton as it travels up the chain, although the situation is confused by the presence of some local phonon modes at the end of the chain. The dimerisation pattern is plotted after 5, 15 and 25 time steps, where the time step is about 1fs as usual. A characteristic soliton velocity of $1.2 \times 10^4 \text{ms}^{-1}$ can be deduced (§6.7 again).

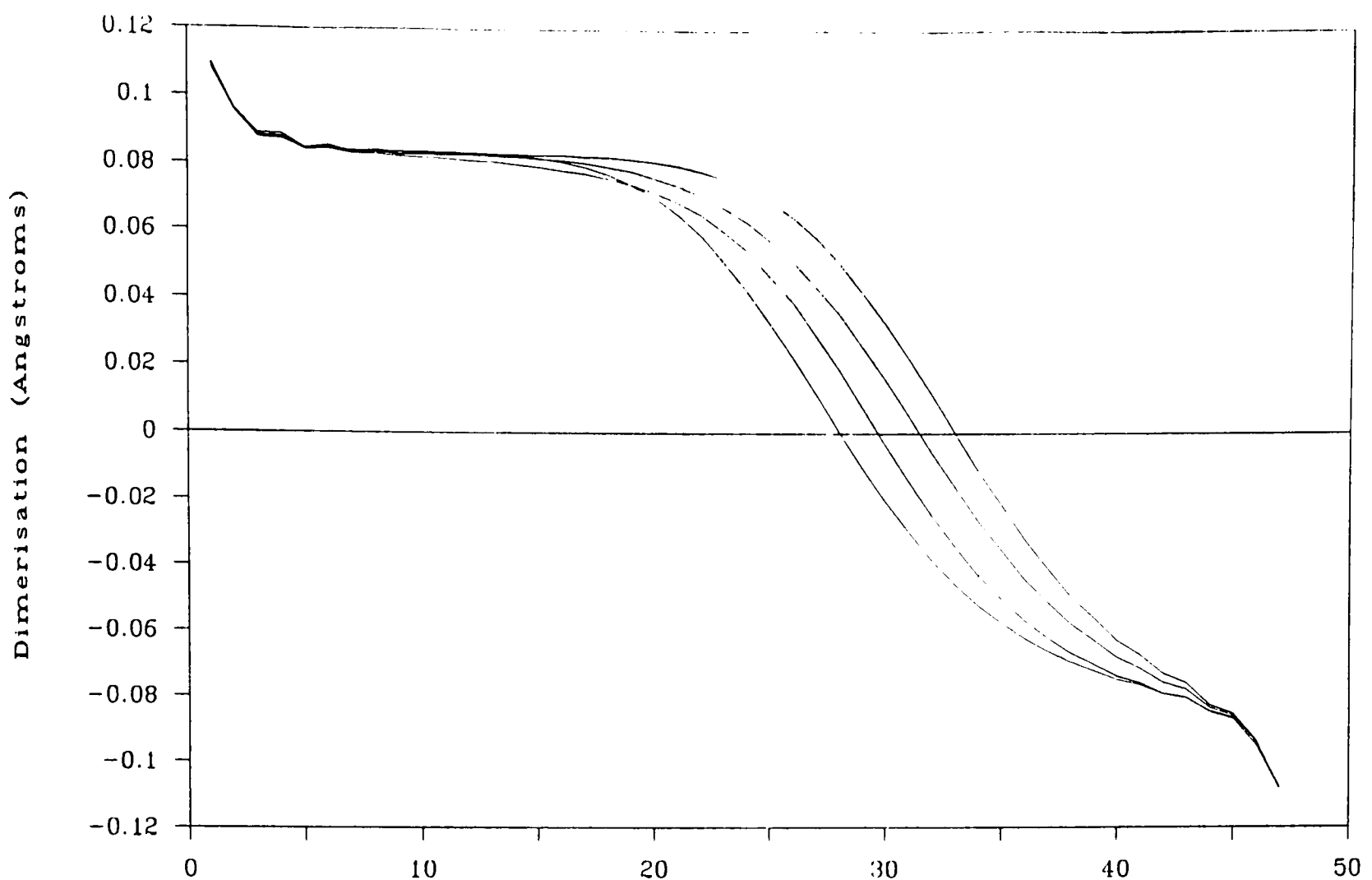


Fig. 6.23 Dimerisation pattern of a chain containing a positively charged soliton, under the action of an electric field. The dimerisation pattern is plotted at four times, each separated by 5 time steps, and the soliton is observed to move along the chain at a velocity which remains constant to a very good approximation, and which is determined by the soliton mobility and the strength of the applied field. In §6.8, a value of $\mu=0.75\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ is derived from these data.

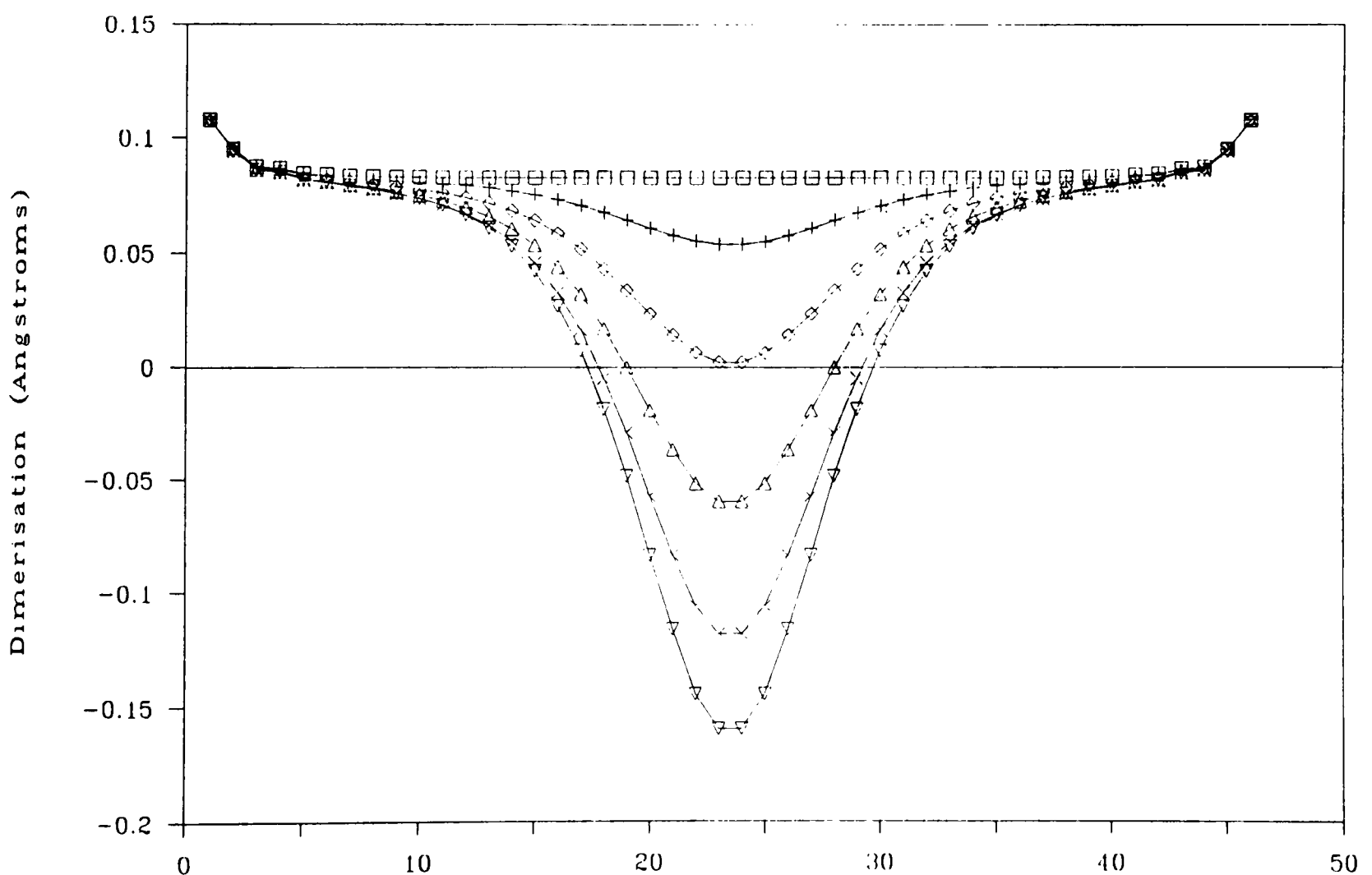


Fig. 6.24(a) Illustration of a breather in t-PA (see §6.9). The dimerisation along a chain is plotted at successive times, after an electron-hole pair is injected at $t=0$. Initially, the chain is uniformly dimerised, but in the four parts of this figure it is seen that the dimerisation resembles that of a bound soliton pair, with a local oscillation of the atoms in the centre of the defect superimposed. The finite time step used here means that the energy appears to be gradually dissipated, but the form of the oscillating defect is clear. The dimerisation pattern is plotted in this part for $t=0$ to 5 time steps:

□: $t=0$ +: $t=1$ ◇: $t=2$ △: $t=3$ ×: $t=4$ ▽: $t=5$

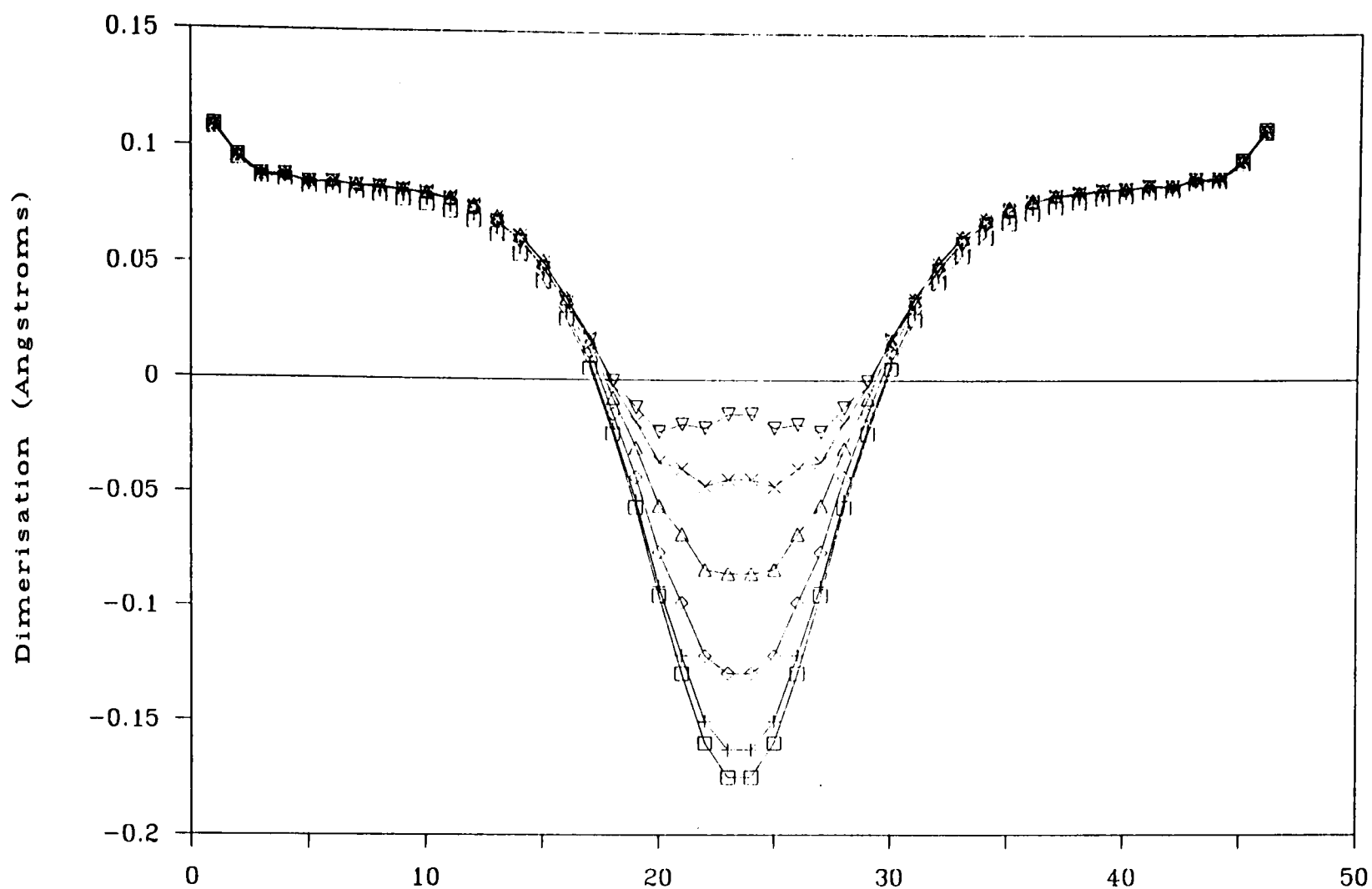


Fig. 6.24(b) As above, with dimerisation plotted for $t=6$ to 11 steps:
 $\square$: $t=6$ $+$: $t=7$ $\diamond$: $t=8$ $\triangle$: $t=9$ $\times$: $t=10$ ∇ : $t=11$

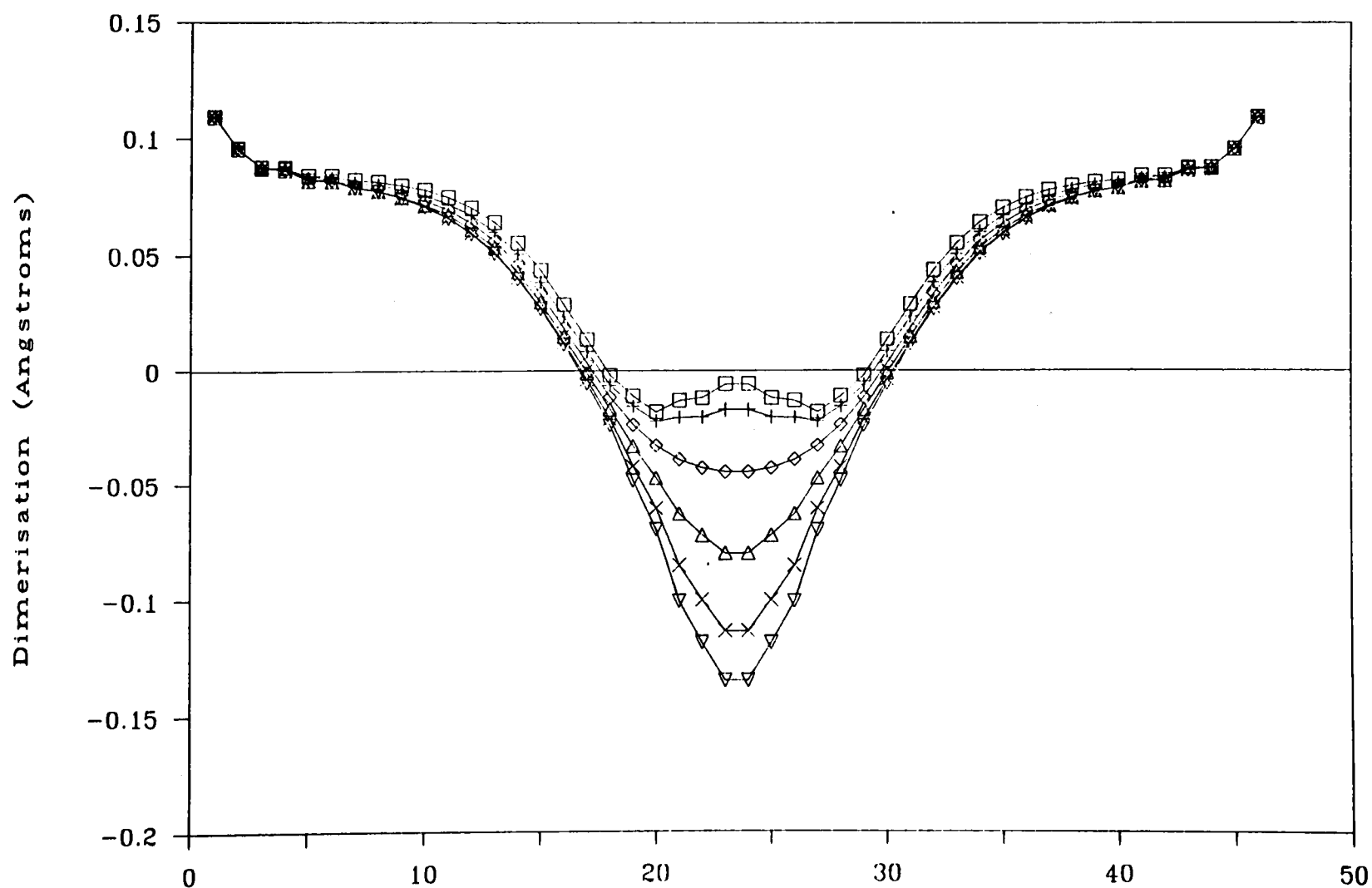


Fig. 6.24(c) As above, with dimerisation plotted for $t=12$ to 17 steps:
 $\square$: $t=12$ $+$: $t=13$ $\diamond$: $t=14$ $\triangle$: $t=15$ $\times$: $t=16$ ∇ : $t=17$

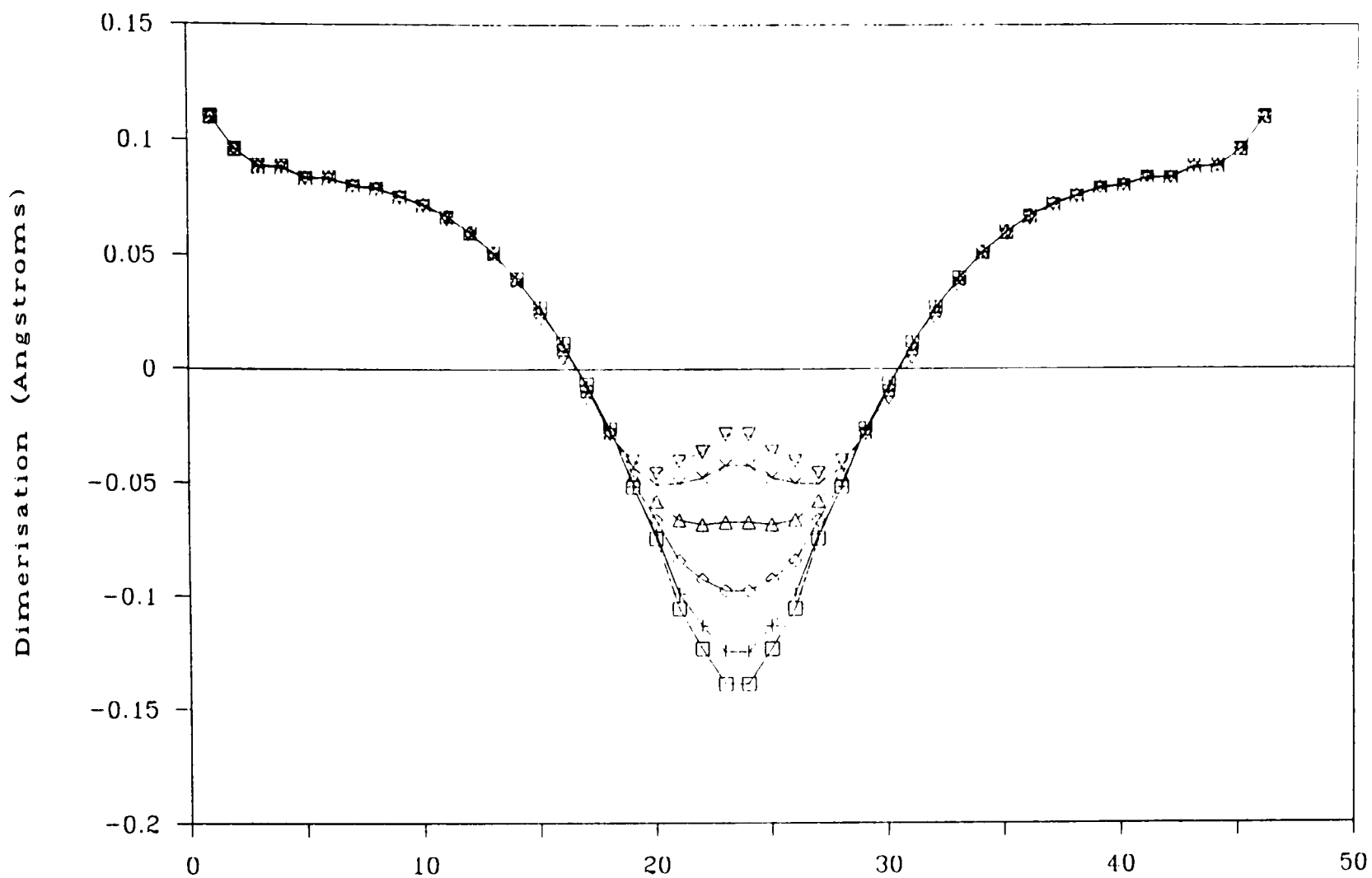


Fig. 6.24(d) As above, with dimerisation plotted for $t=18$ to 23 steps:
 $\square$: $t=18$ $+$: $t=19$ $\diamond$: $t=20$ $\triangle$: $t=21$ $\times$: $t=22$ ∇ : $t=23$

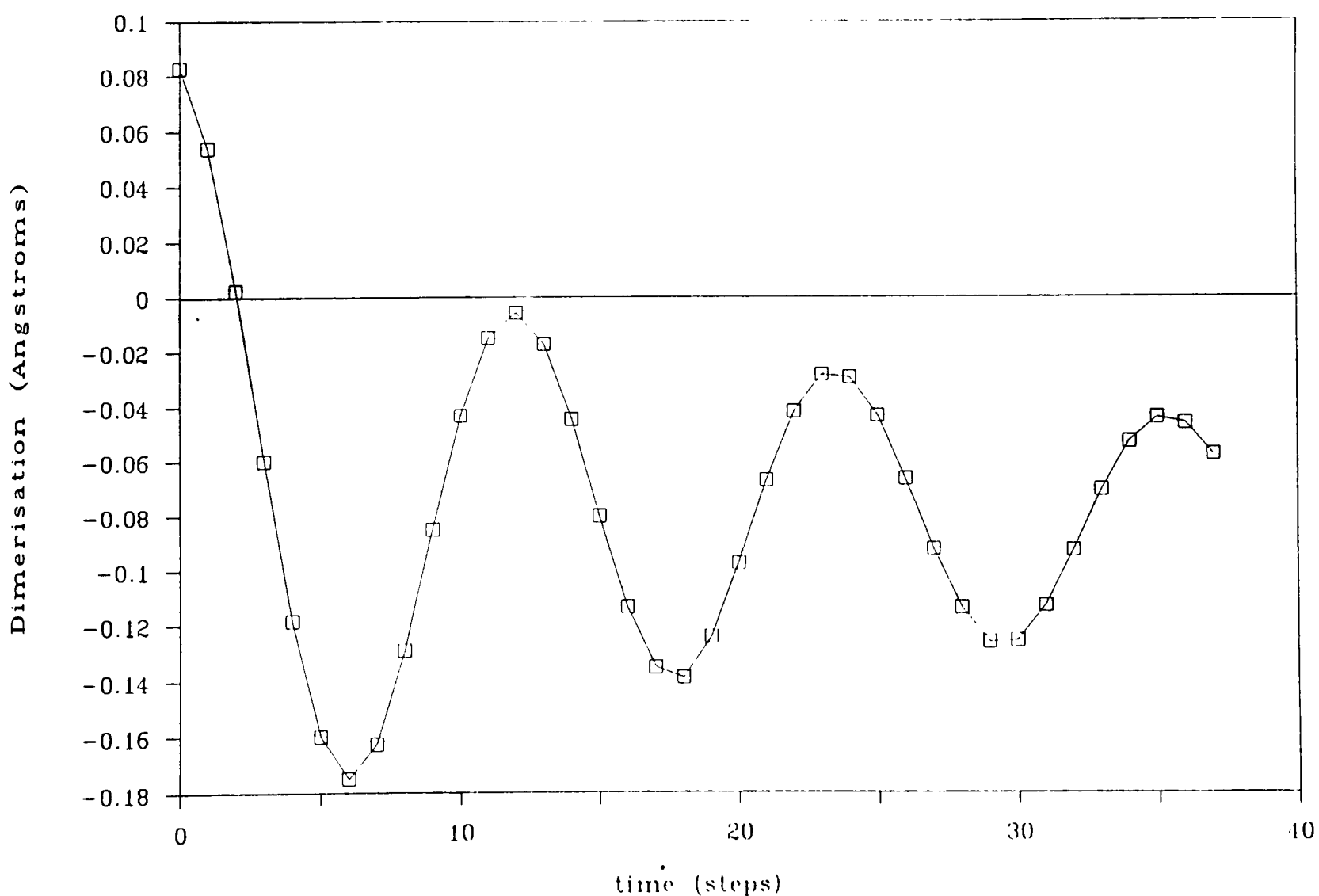


Fig. 6.25 Demonstration that the oscillation of the bonds at the centre of the breather is periodic. Plotted is the dimerisation at the centre of the chain against time, and although the motion is dissipated slightly, its periodic nature is clear; the frequency is very similar to that of the LO Raman mode (see §§6.6 and 6.9), to which the breather is strongly coupled.

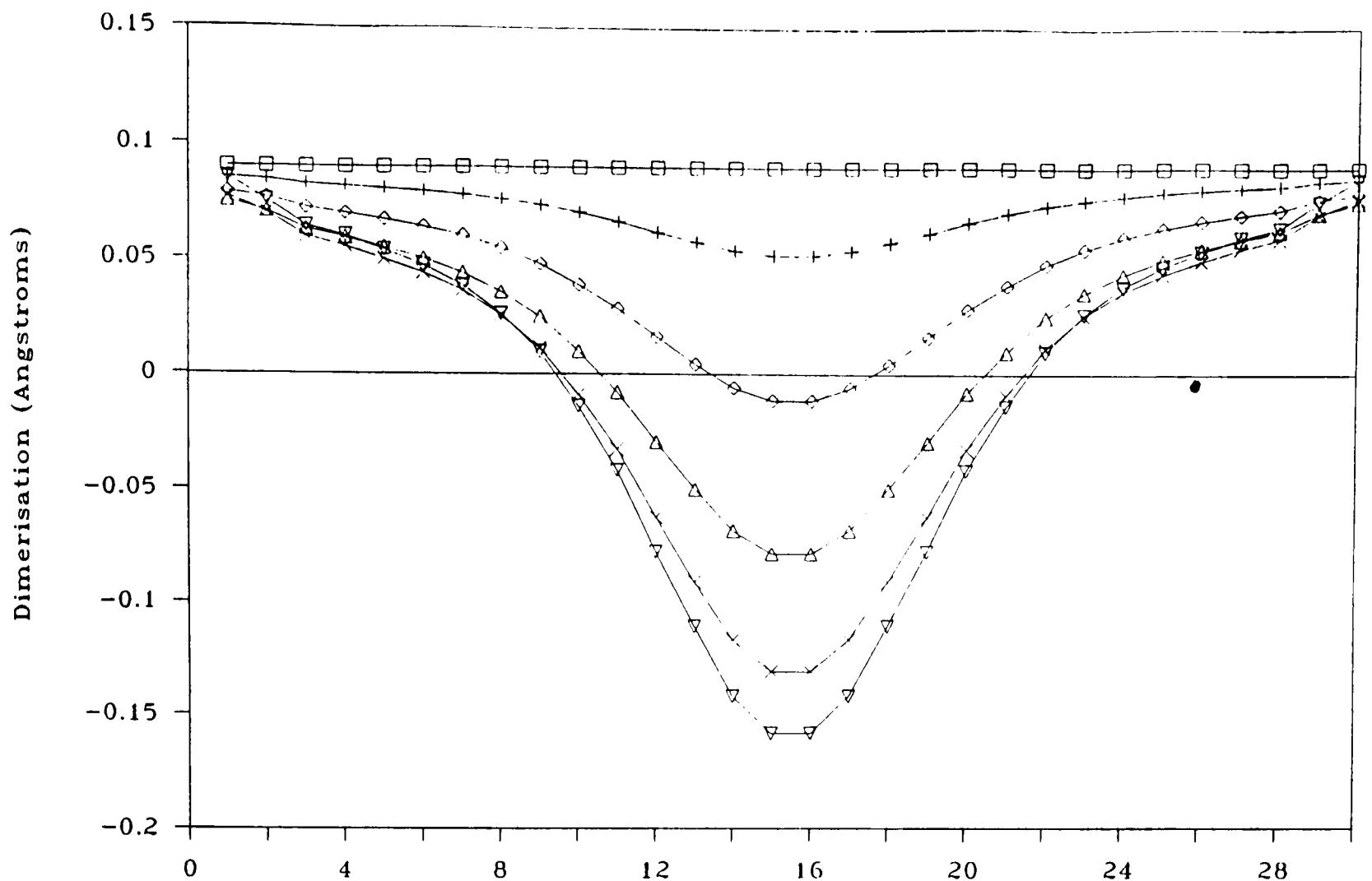


Fig. 6.26 Behaviour of a c-PA chain on injection of an electron-hole pair. For $t=0$ to 5 steps, the behaviour is similar to that of t-PA under the same conditions (fig.6.23(a)). The dimerisation is plotted here for these times:

□: $t=0$ +: $t=1$ ◇: $t=2$ △: $t=3$ ×: $t=4$ ▽: $t=5$

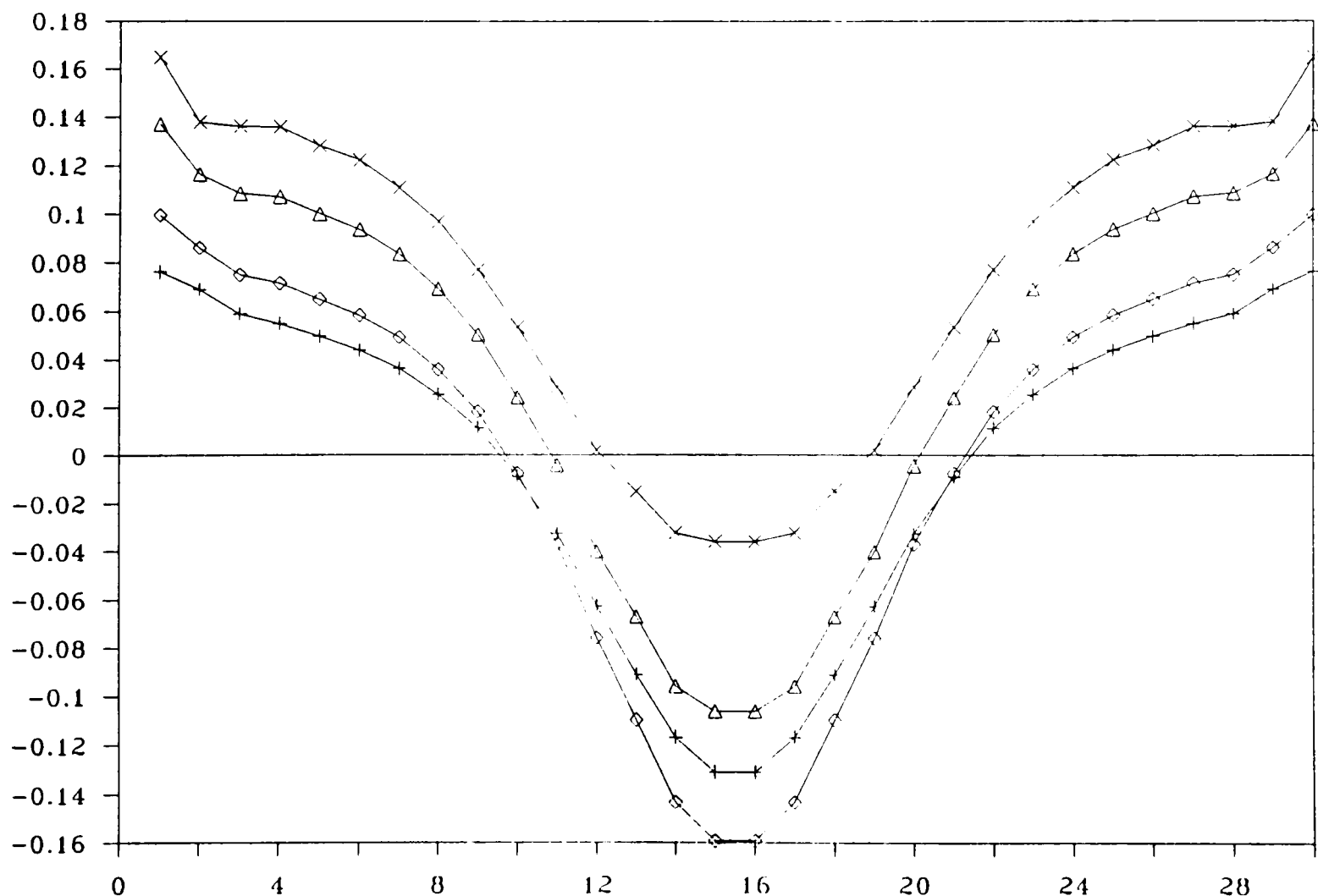


Fig. 6.27 Demonstration that the breather is not a stable excitation in c-PA. The dimerisation pattern is plotted here for $t=4$ to 10 steps, and it is clear that the oscillation takes the form of an exciton (equivalent to the bound soliton pair in t-PA) with an oscillation of the dimerisation of the *whole* chain superimposed. This just represents the LO mode, and it is this vibration that is excited, rather than the strictly localised mode characteristic of the breather.

+: $t=4$ ◇: $t=6$ △: $t=8$ ×: $t=10$

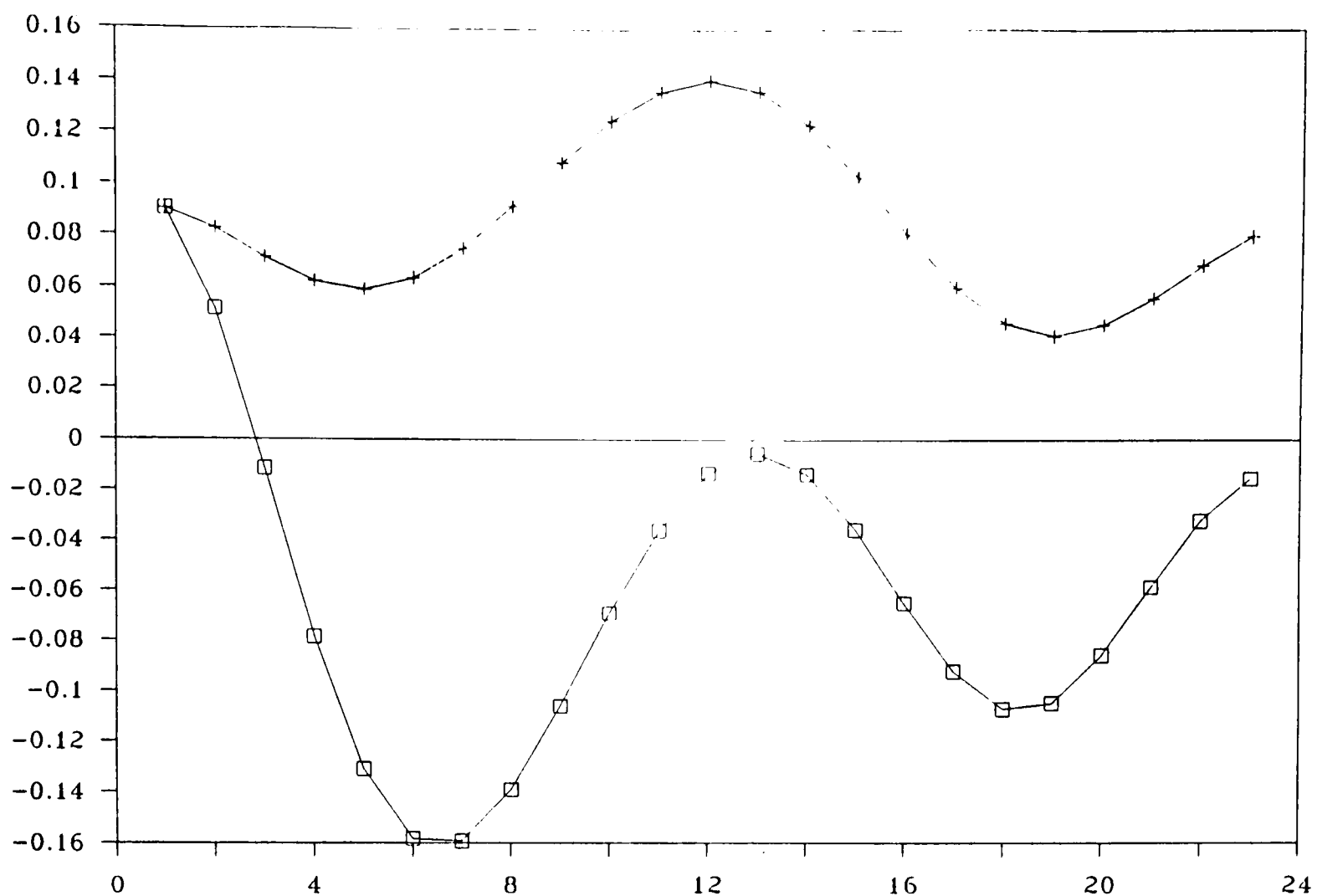


Fig. 6.28 Indication of the change from localised to global vibration. The dimerisation at the centre of the chain (squares), and at a position near the end of the chain (crosses), are plotted against time. Initially, the two dimerisations separate, but after about 10 time steps (i.e. 10^{-14} s) they begin to oscillate in unison, representing the LO mode.

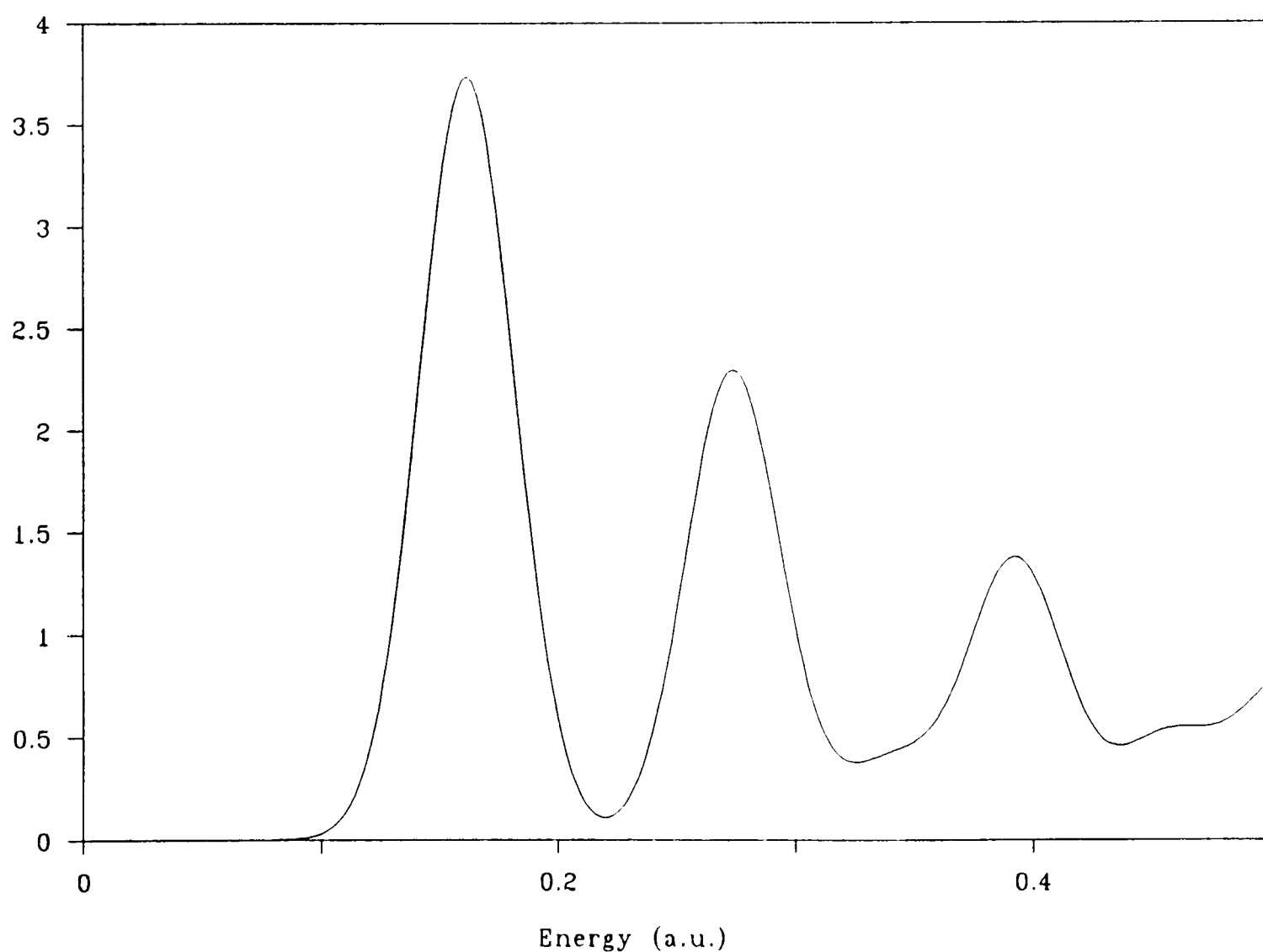


Fig. 6.29 Low-energy calculated optical absorption of t-PA, using a molecule of $C_{24}H_{26}$ as a model (see §6.10). The absorption appears to consist of four main peaks (the tail of the fourth can be seen at the high-energy end of the graph), but this is not a genuine result, merely an artefact of the calculation being performed on one, fairly short chain. Hence the absorption peaks are spaced well apart (because of the short length), and there is an absence of any smearing due to a mixture of chain lengths, as would be observed in experiment.

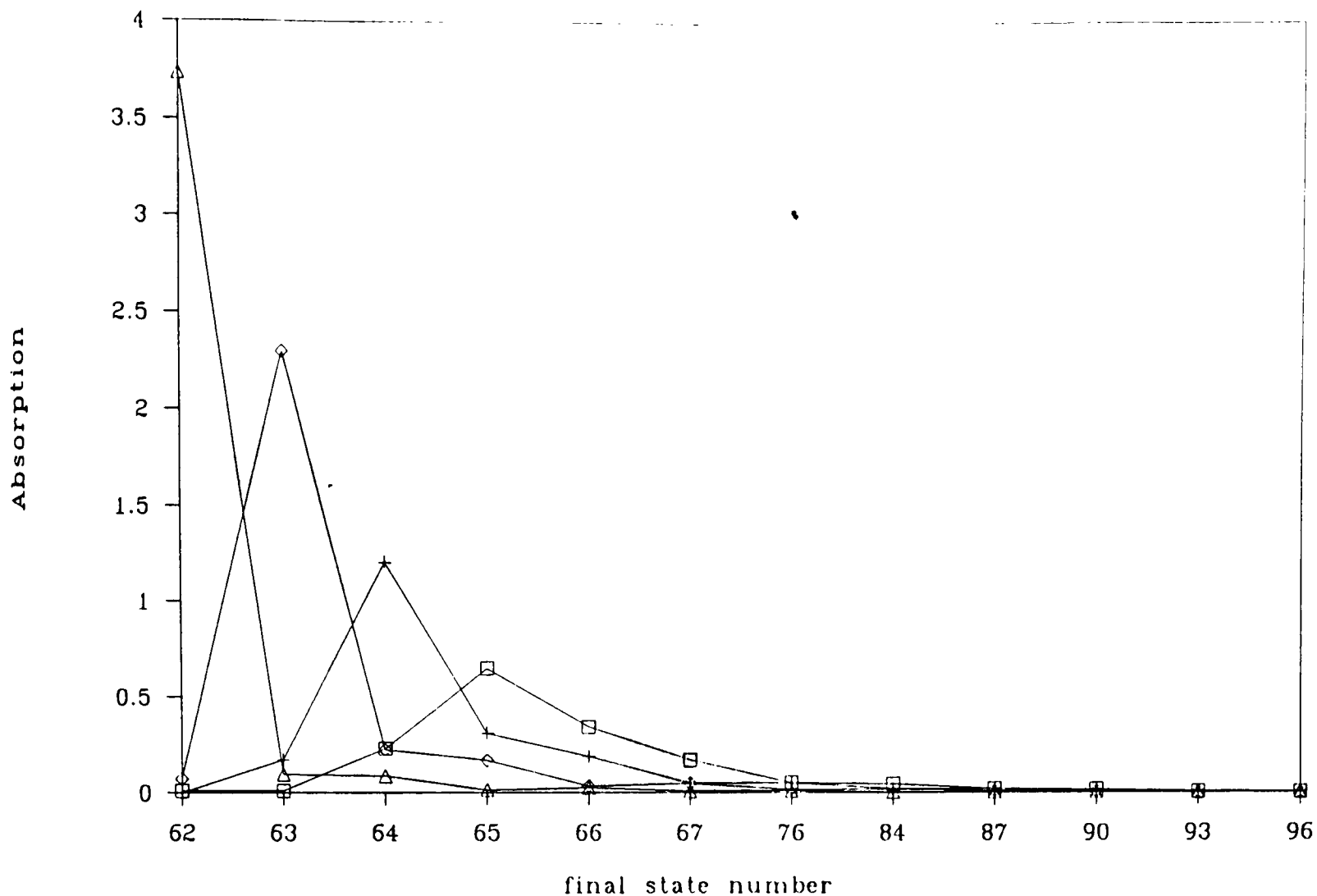


Fig. 6.30 Optical absorption weights from the four highest valence band π states of trans- $C_{24}H_{26}$ to the conduction band states. Note that each of the V.B. states is associated with one particular C.B. state, which is its charge conjugate pair. Note also that the conduction band π^* states are not the twelve lowest C.B. states (which are numbered in order of increasing energy), but that the very edge of the conduction band, which is where most of the interesting absorption will occur, is made up of π^* states.

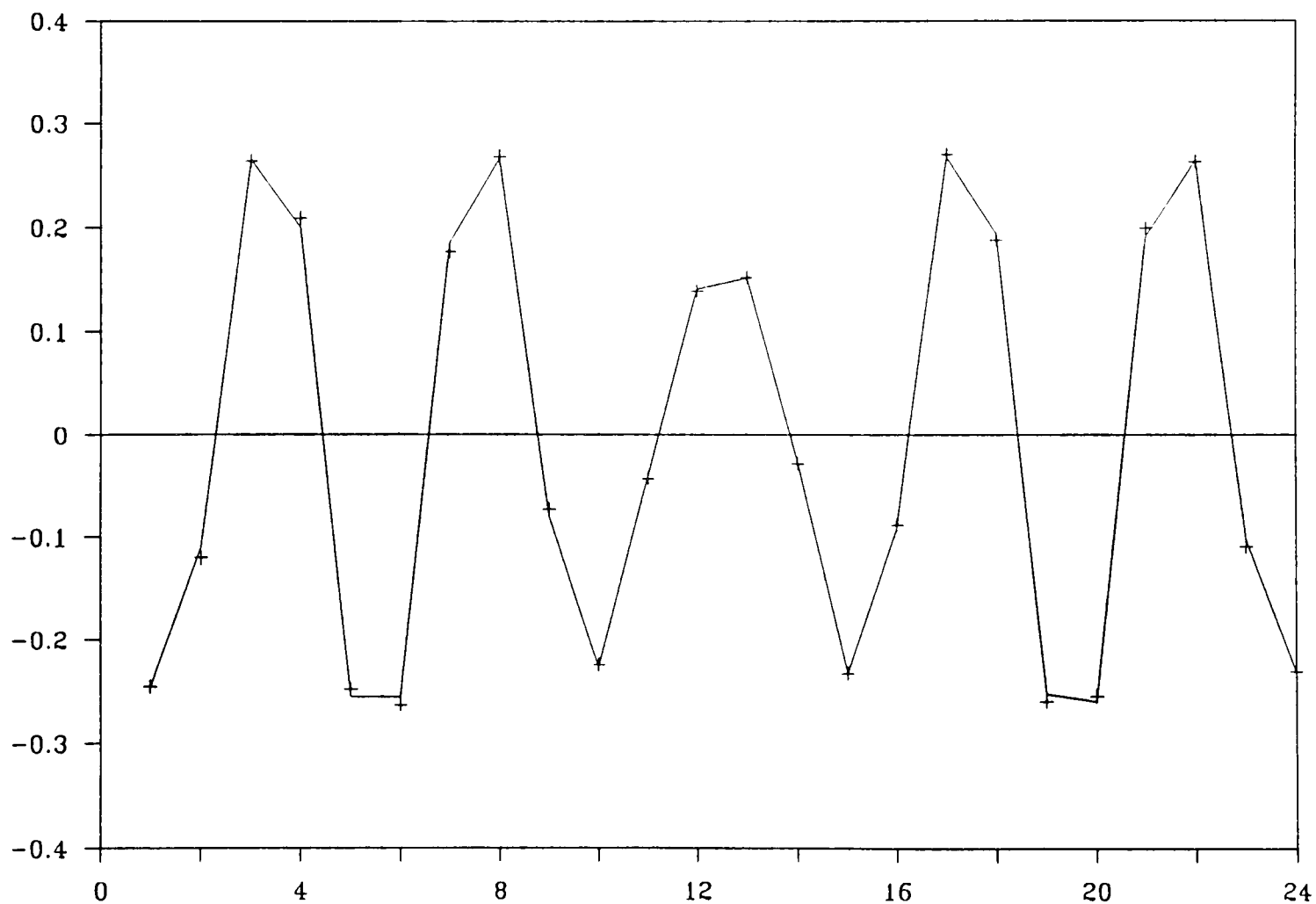


Fig. 6.31 Demonstration of the charge conjugation pairing of eigenstates. The quantity plotted is the component of the n 'th atomic p_z orbital in a given molecular orbital; the solid line joins the values appropriate to the second orbital from the top of the valence band, and the crosses are the values for the second state from the bottom of the conduction band, but with a factor $(-1)^n$, representing the charge conjugation operator. An equivalent result is obtained for all of the π and π^* states; the states plotted here are used solely as an example. Note, however, that charge conjugation pairing of the eigenstates is *not* a test of CCS; see §6.10.

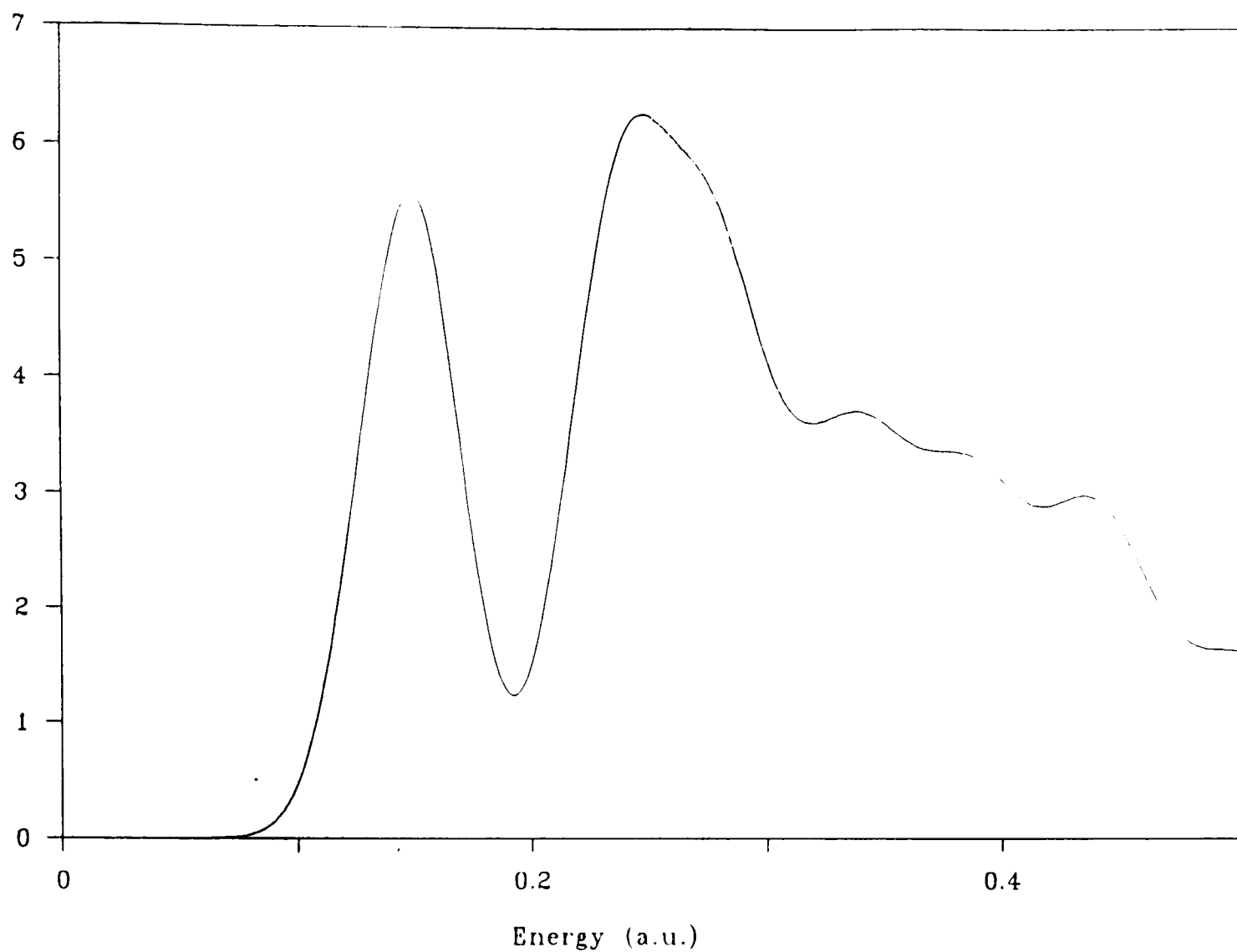


Fig. 6.32 Calculated optical absorption of t-PA with a charged soliton. The presence of one absorption peak within the gap is clearly seen; any structure in the interband absorption is probably fictitious.

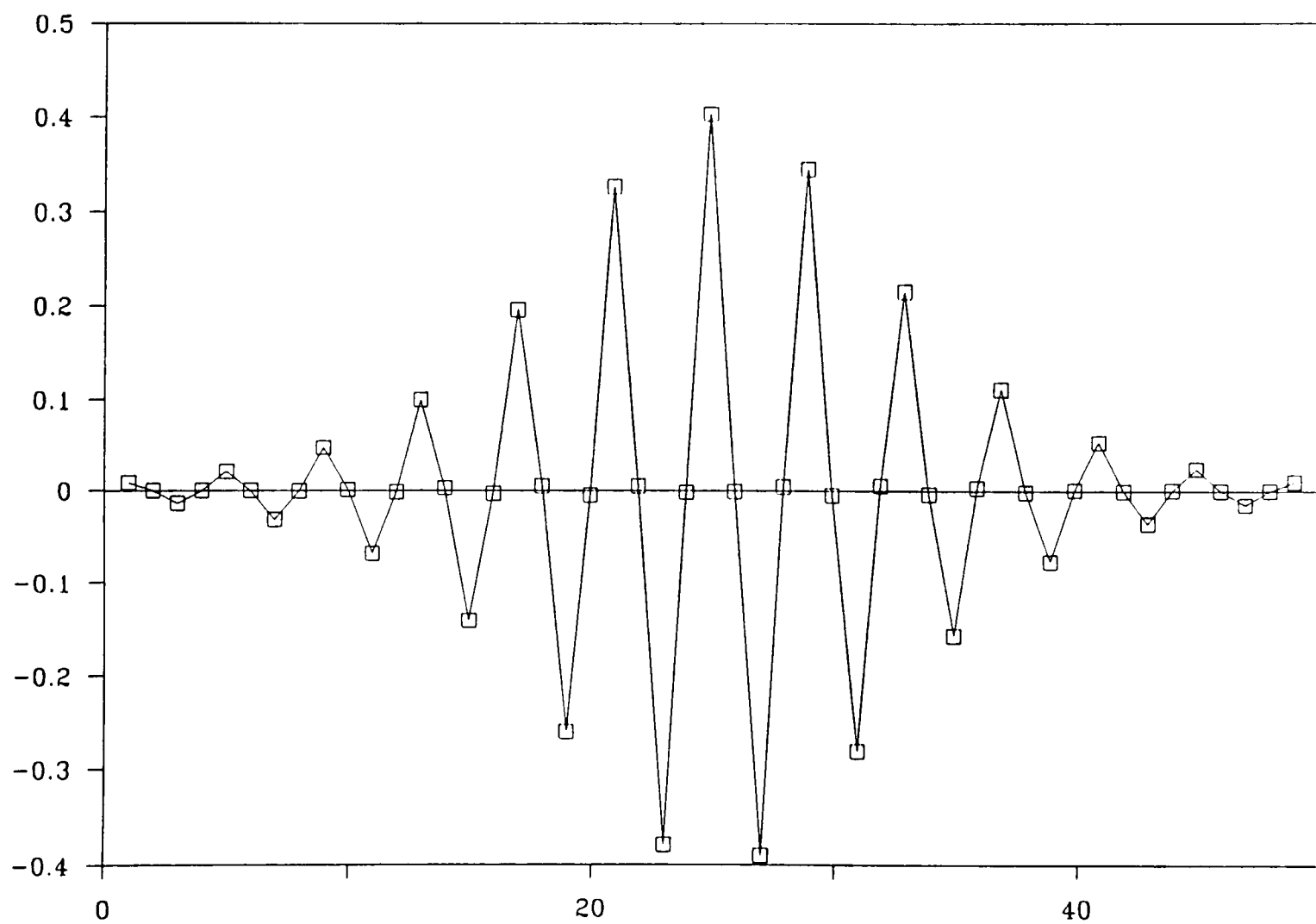


Fig. 6.33 Wave function of a soliton state. Note that the state has approximately zero amplitude at each alternate site; this is a prediction of CCS, but is still supported even when the symmetry is not in force.

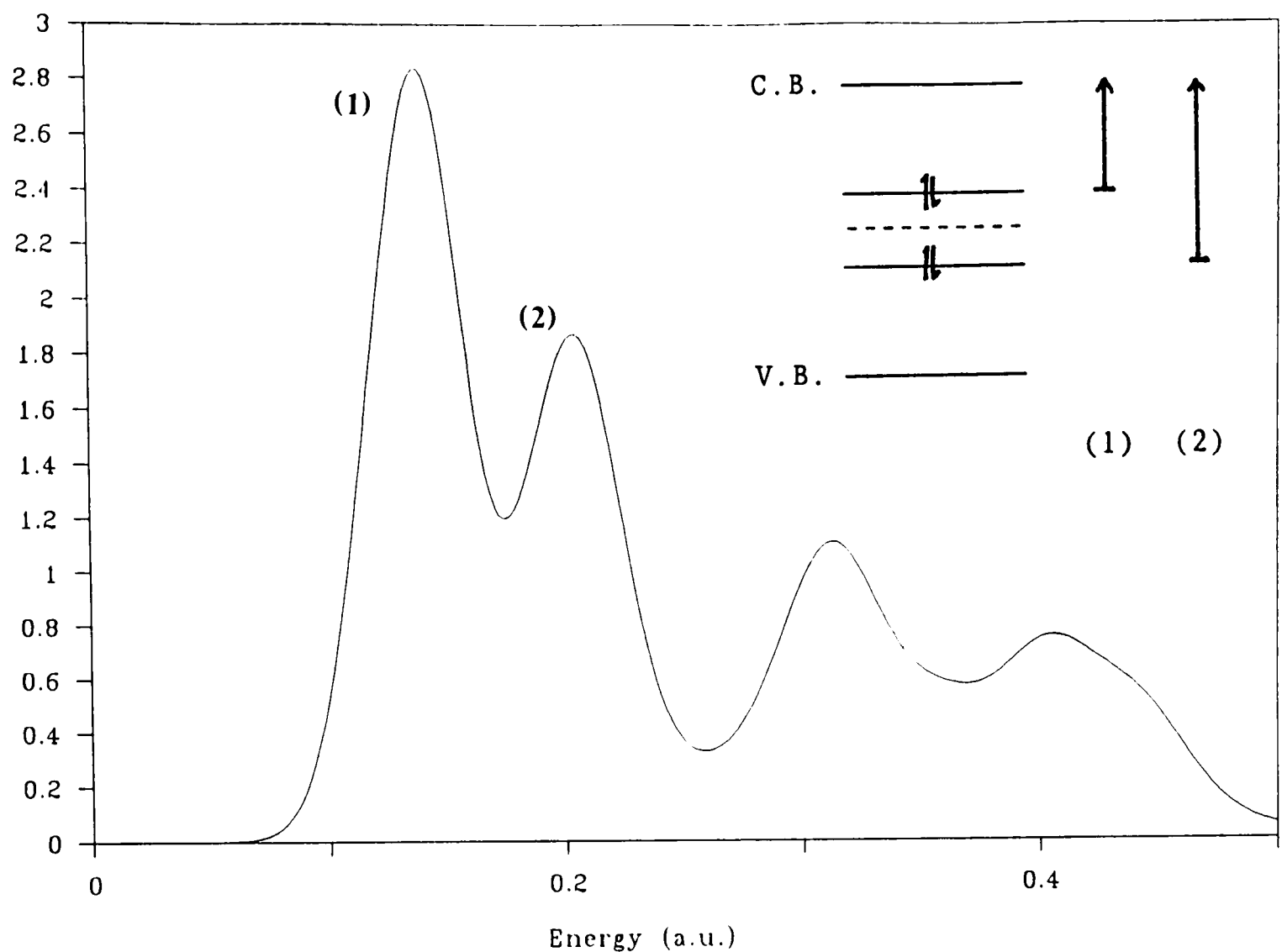


Fig. 6.34 Calculated absorption of c-PA with a bipolaron. The two peaks of lowest energy correspond to transitions involving the localised states, as shown on the inset diagram; the remainder of the spectrum is due to interband absorption, which appears to show some structure due to the use of a finite chain for the calculation. Note that the ratio between the strengths of peaks (1) and (2) is about 1.5, in contrast to the SSH prediction of about 20.

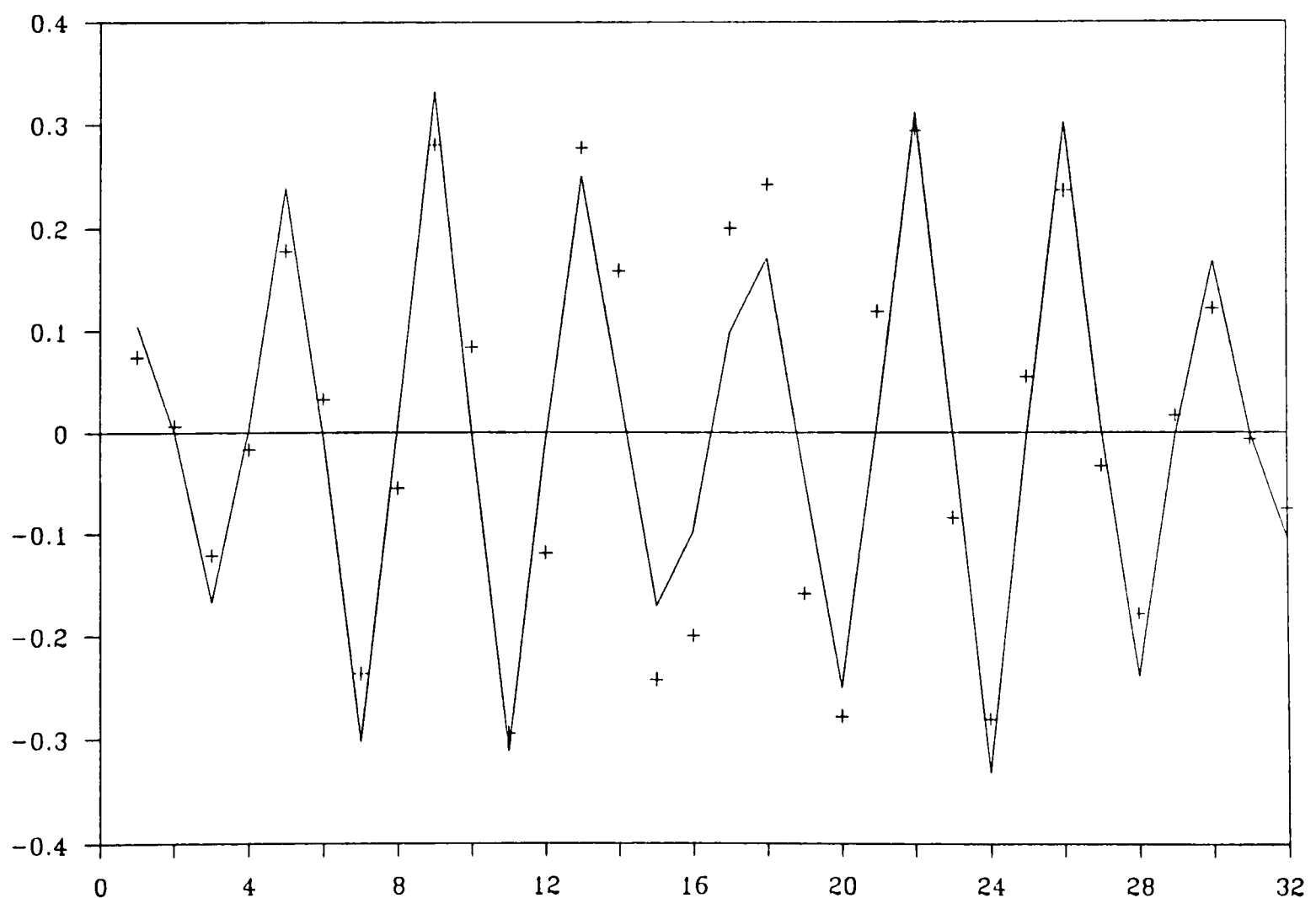


Fig. 6.35 Eigenstates of a c-PA chain with a bipolaron. The solid line corresponds to the lower localised state, while the crosses represent the effect of the charge conjugation operator, which takes $a_{nk} \rightarrow (-1)^n a_{nk}$, on the higher localised state (c.f. fig. 6.31). The two sets of data do not coincide, meaning that the two localised states do not form a charge conjugate pair, i.e. that CCS has been violated.

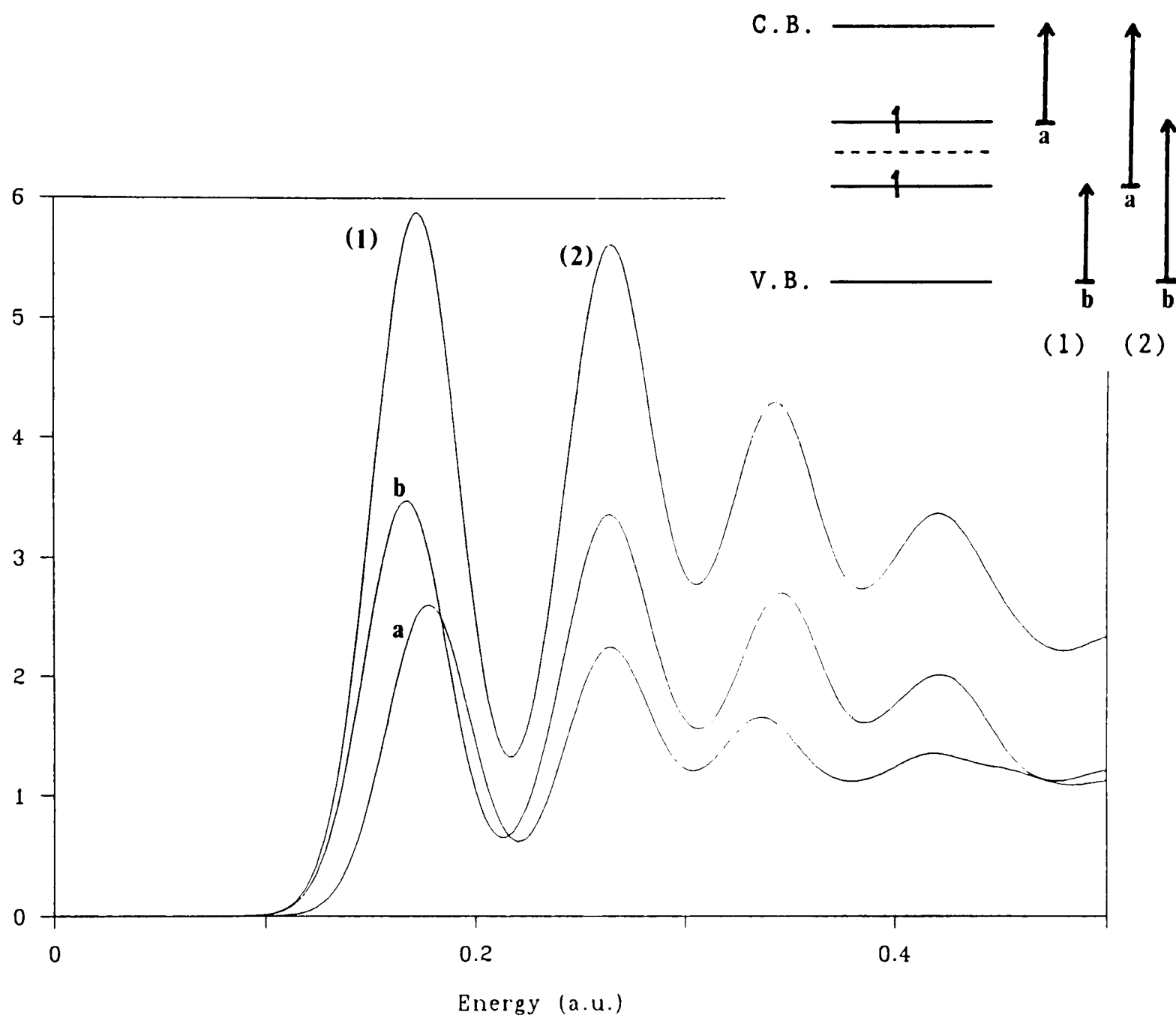


Fig. 6.36 Calculated absorption of c-PA with a triplet exciton. Absorptions due to electronic states of each spin are shown, with the lowest curve representing the spin up absorption and the middle curve the spin down. The higher curve is the sum of these. Although the absorptions for each spin do not occur at precisely the same energy, the energies are so close that they appear to merge into one peak. The peaks are labelled as for fig. 6.34.

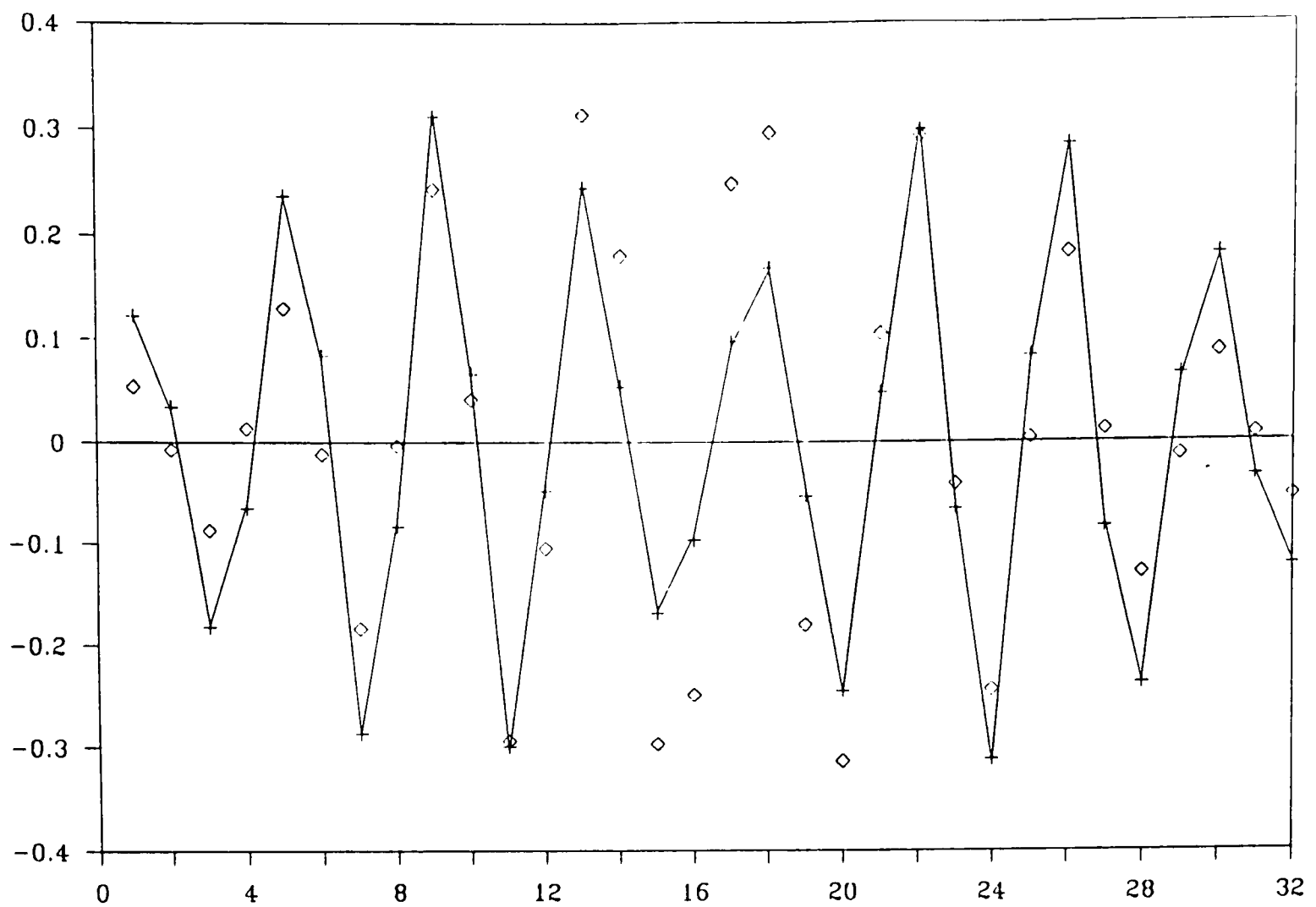


Fig. 6.37 Eigenstates of c-PA with an exciton. The solid line represents the lower localized state of spin up; the squares represent the effect of the charge conjugation operator on the higher localized state of the same spin. These data do not coincide, meaning that the two states are not charge conjugate pairs, but when the charge conjugation operator is applied to the higher localized state of spin *down* (represented by the crosses), the data do coincide. Hence the lower localized state of spin up and the higher localized state of spin down are, in a sense, charge conjugate pairs.

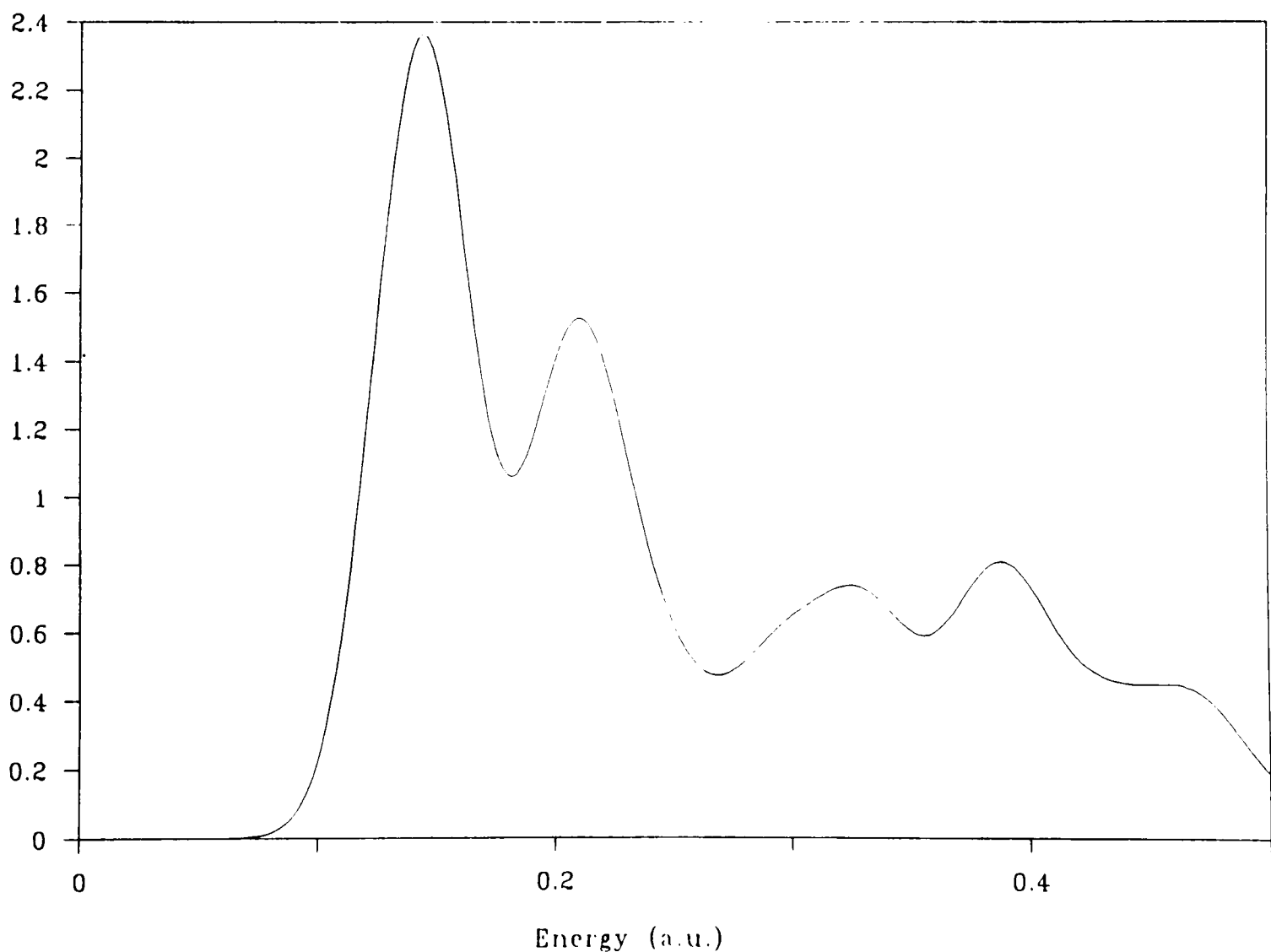


Fig. 6.38 Calculated absorption of PT with a bipolaron. The absorption within the gap consists of two peaks, again with strengths in the ratio 1.5:1. SSH predicts a ratio of about 12 in this case.

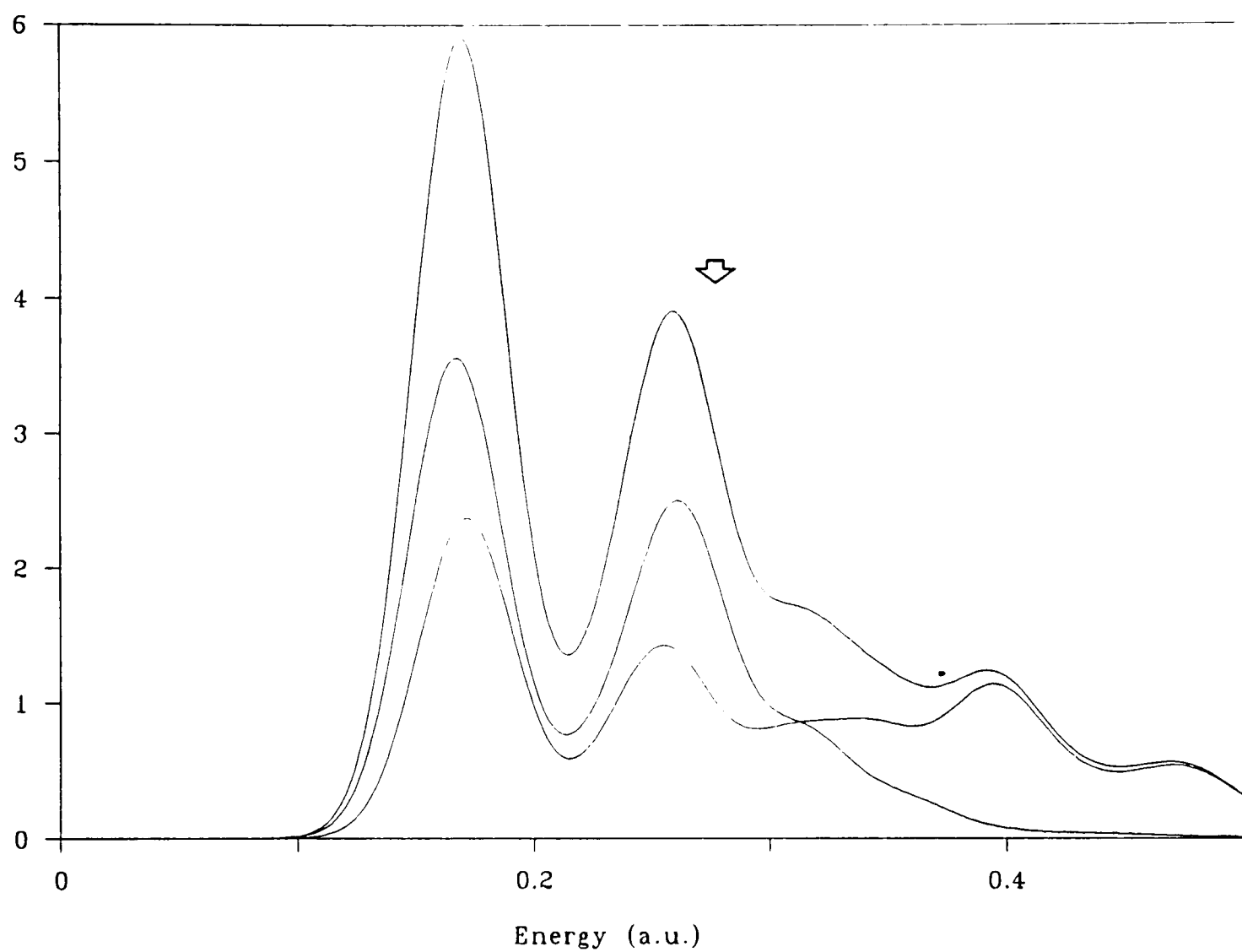


Fig. 6.39 Calculated absorption of PT with a triplet exciton. The lowest curve represents the spin up absorption as for fig. 6.36. Here the interband absorption is so weak that it appears almost to be a tail of the higher energy localised state transition. The energy of the lowest interband transition is marked with an arrow on the figure.

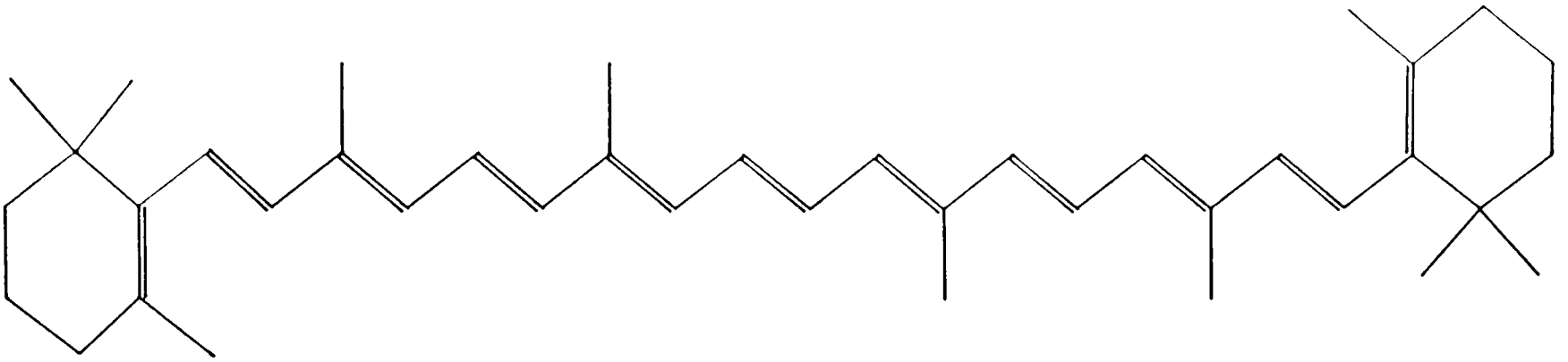


Fig. 6.40 Structural formula of β -carotene (see §6.11). The long central conjugated section means that it may mimic some of the properties of conjugated polymers.

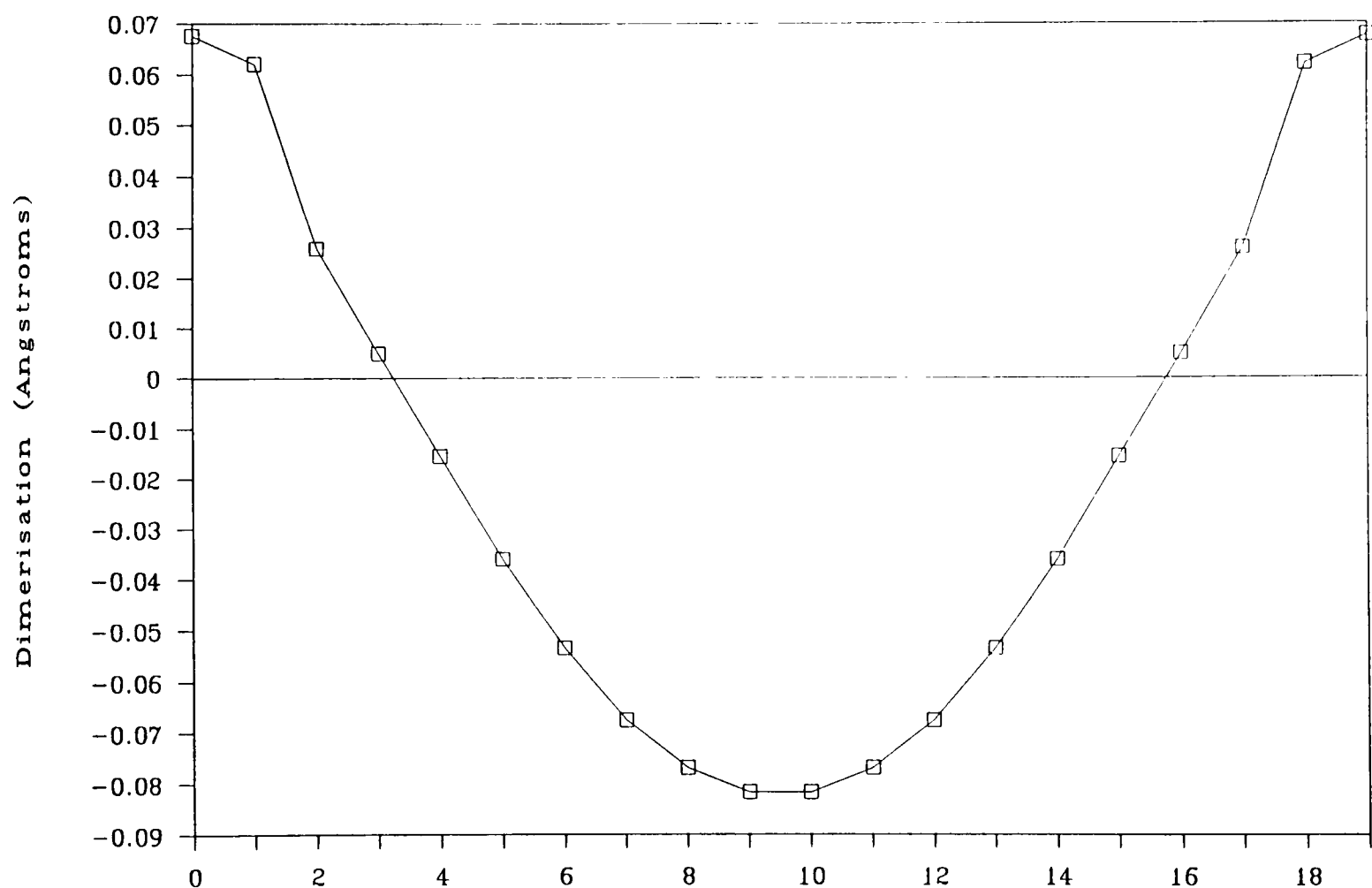


Fig. 6.41 Dimerisation pattern of an exciton in β -carotene. The dimerisation is defined in the same way as for the conjugated polymers, with the entire conjugated section of the molecule being considered. Although the chain is too short for the defect to spread out as much as it would in a longer chain, its shape is very similar to that of an exciton in polyacetylene (see fig. 6.12).

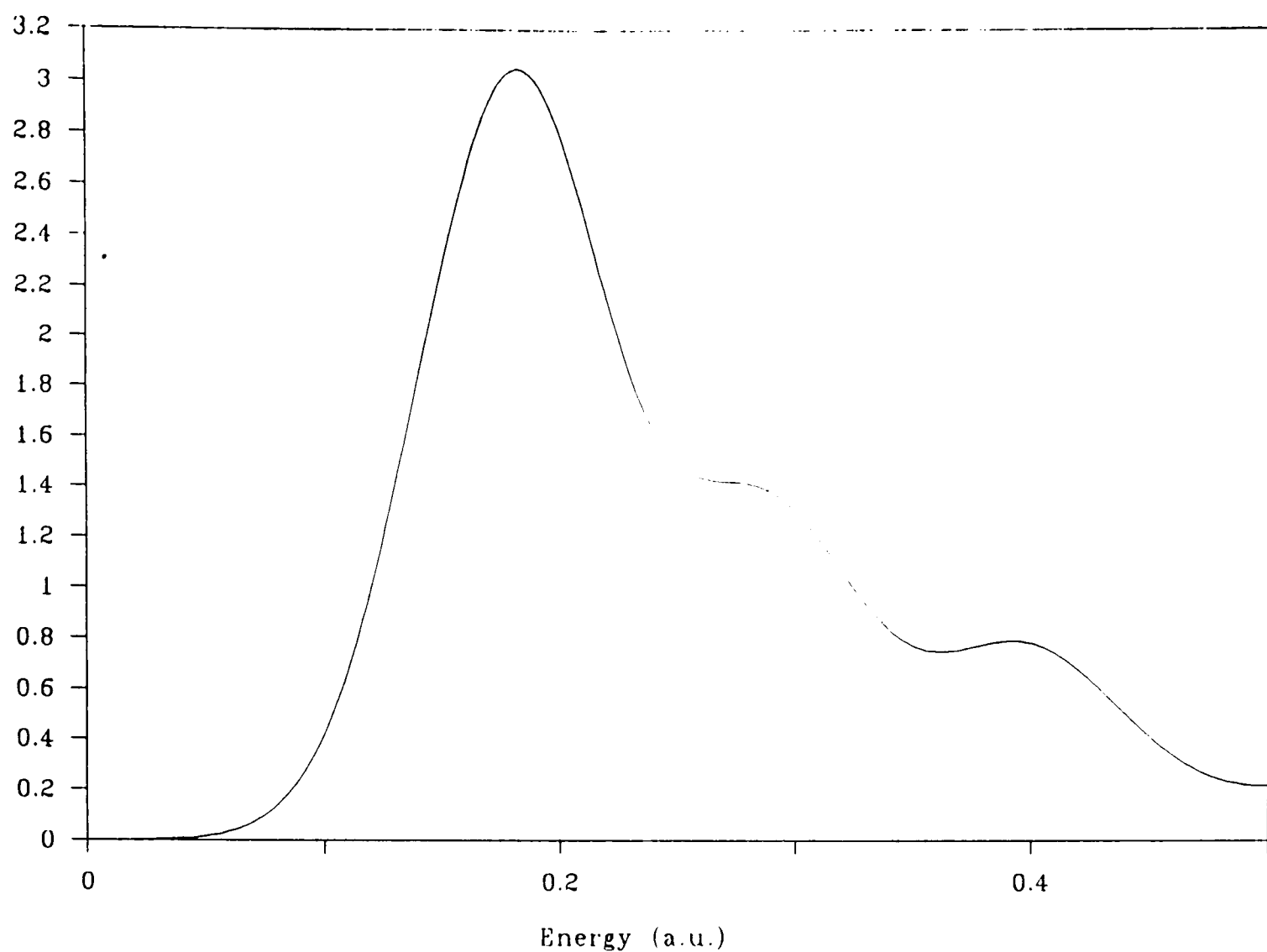


Fig. 6.42 Calculated ground state optical absorption of β -carotene near the band gap. All of the absorption shown is due to $\pi \rightarrow \pi^*$ transitions.

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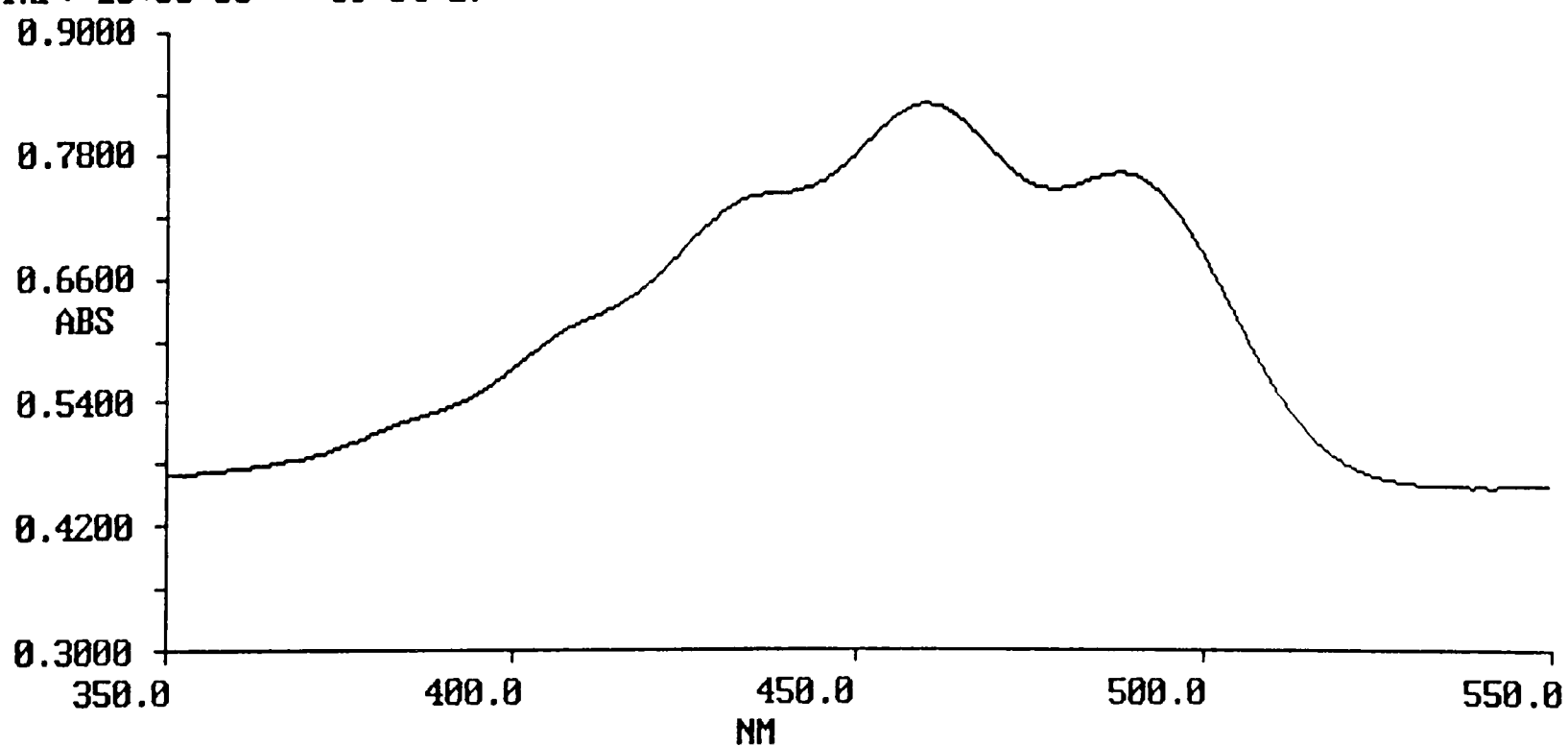


Fig. 6.43 Experimental optical absorption of β -carotene. A number of peaks are observed above the band gap, as in the calculated absorption, although their weights differ slightly from those predicted.

7.1 INTRODUCTION

It has been stated earlier that one of the shortfalls of the SSH model is its failure to account for the low quantum yield of photoluminescence in c-PA (Hayes *et al.* 1983, Andrews *et al.* 1983); the SSH model Hamiltonian displays charge conjugation symmetry (CCS), which forbids non-radiative decay from a photoexcited state to the ground state (Danielsen and Ball 1985), and it has always been assumed (Hayes 1985) that the low efficiency of luminescence is due to a competing non-radiative transition, in violation of this symmetry. Various authors (Sum *et al.* 1988, Danielsen and Ball 1985) have suggested possible mechanisms for this symmetry breaking, but the use of CNDO in place of SSH as a method automatically breaks the symmetry, as evidenced by calculations of optical absorption weights performed in §6.10, so the question of how to model this CCS breaking within SSH no longer needs to be considered. The photoluminescence of c-PA is still an area worth study, however, since it will become clear that straightforward competition from a non-radiative decay mode will not explain all of the observed features.

7.2 EXPERIMENTAL OBSERVATIONS

The spectrum of scattered light from photoexcited c-PA consists of a broad luminescence peak centred at 1.9eV, with a multiple overtone Raman spectrum superimposed (Lauchlan *et al.* 1981). The luminescence requires an excitation energy of 2.05eV and has a low quantum efficiency of at most 10^{-5} .

Shank *et al.* (1982) studied the time dependence of the 1.6eV photoinduced absorption peak of c-PA, the higher in energy of the two peaks observed within the band gap. They found that the absorption consisted of two components: one short-lived, with a decay time of order picoseconds, and one long-lived, with a lifetime of at least some milliseconds. The

frequency profiles of these two components were identical, implying that they arose from the same source, and their intensities were comparable, with the short-lived component having roughly double the strength of the long-lived. The absorption appeared to start immediately upon excitation, which with their resolution implied a formation time for the species responsible of less than 150fs.

In addition to directly observing a 9ps upper limit for the luminescence lifetime, Hayes *et al.* (1983) argued that the data of Shank *et al.* implied an upper limit of 150fs, since no change to the photoinduced absorption was observed on this time scale.

The difference between the required excitation energy and the energy of the luminescence appears to imply a Stokes shift of $\approx 0.15\text{eV}$, but doubts over this interpretation have been raised by Tubino *et al.* (1984) and by Andrews *et al.* (1983). The former claimed that this energy difference was not a Stokes shift as such, but arose from some shallow gap state, about whose nature they did not speculate; the latter calculated the transition moment required to account for the observed luminescence and found that the short lifetime required an unexpectedly large transition moment even for such a low quantum efficiency.

7.3 COMPARISON WITH THEORY

Calculation of the Huang-Rhys factor for a polaron-like defect in PA gives a value which depends on the shape of the distortion pattern, as well as on its amplitude. However, the dependence on the defect shape is fairly weak (see Appendix 1.2), so to a first approximation the defect depth can be treated as the most important parameter. Defining α , a measure of this depth, to be the ratio of the maximum change in the dimerisation parameter to its ground state value d_0 :

$$\alpha = \frac{|d_n - d_0|_{\text{max}}}{d_0},$$

and using typical values for the parameters which define the defect shape,

a Huang-Rhys factor of $S_0 \approx 2\alpha^2$ is found (see Appendix 1.2). Values of α can be found by self-consistent geometry minimisation in either the SSH or semi-empirical Hartree-Fock models, and for an exciton in c-PA these methods lead to values of 1.05 and 1.8 respectively. Since the Stokes shift is equal to $2S_0\hbar\omega$, and the phonon energy $\hbar\omega$ is 0.18eV in c-PA (Lefrant *et al.* 1979), it is clear that, if the apparent Stokes shift of 0.15eV is genuine, there is a discrepancy between theory and experiment of about an order of magnitude.

It can be confirmed that this discrepancy is not due to any of the approximations involved in calculating the Huang-Rhys factor by looking at the results of explicit calculations, within the SSH model, of the energies of various defects. The energy saved by lattice relaxation around a polaron in c-PA is 0.08eV (see §1.5), in good agreement with the calculated value of $\alpha \approx 0.4$ (fig. 2.15). For a bipolaron, which is equivalent to an exciton in the SSH model (by charge conjugation symmetry - see §3.6), the equivalent energy is 0.43eV, again in good agreement with the calculated defect depth $\alpha \approx 1.05$ (fig. 2.17).

Within CNDO, constraining a system to remain in an excited state is not so easy, and the calculations for an exciton were performed on the triplet state, the accuracy of the calculations relying on the energy splitting between equivalent (excited) singlet and triplet states not being too great. Relative to the ground state energy, the following values were obtained:

Triplet energy at ground state geometry = 3.668eV

Triplet energy (relaxed) = 1.729eV

"Ground state" energy at triplet geometry = 2.211eV

It can be seen that the relaxation energy of the exciton is 1.939eV, fairly close to the lattice energy of the ground state at the exciton geometry, implying that the vibrational mode frequencies do not change by too much on photoexcitation. Note that CNDO is primarily a method for calculating good

molecular geometries rather than good energies; it tends to over-predict energies (notably phonon energies), and the values quoted above might easily all be too large by a factor of 2. Given that the phonon energies will be over-predicted as always, it will only be possible to predict the defect geometry correctly if the band gap (i.e. the triplet energy at the ground state geometry) is also over-predicted. This is the case here, so it is possible to have some confidence in the calculated configuration co-ordinate curves shown below.

It does appear from both SSH and CNDO calculations that the observed Stokes shift is substantially lower than predicted theoretically, and an explanation for this may be found in the very short lifetime of the luminescence. This would imply that the observed luminescence is actually *hot* luminescence, occurring before the chain has had time to reach its equilibrium geometry; although hot luminescence has not been considered in c-PA, it has been claimed by Lauchlan *et al.* (1983) that it is important in t-PA.

Configuration co-ordinate diagrams for c-PA within the SSH and CNDO models (fig. 7.1) yield some very interesting results. The chain energy has been plotted as a function of the defect depth α , assuming harmonicity and (for the SSH model) that there is no change in vibrational frequency on photoexcitation. With these assumptions, enough is known from calculations of the geometries and energies of the ground and excited states to enable these diagrams to be drawn.

SSH MODEL. The common assumption that luminescence quenching is due to a competing non-radiative process is found to be unsupportable within the SSH model. This is because non-radiative decay is forbidden not only by symmetry, but also because the crossover between the ground state and excited state energy curves occurs at significantly *higher* energy than the vertical excitation energy, and thus there is no way that the geometry necessary for the proposed non-radiative transition to take place can ever

be attained. The SSH model therefore predicts 100% luminescence, irrespective of any symmetries that may or may not forbid non-radiative decay. Clearly this result is in complete disagreement with experiment, and the reason for this discrepancy will be discussed below.

CNDO MODEL. Within CNDO, it is the position of the energy minimum of the excited curve that is most interesting; it actually occurs just *outside* the ground state energy curve. Once the excited state has reached its relaxed geometry, therefore, a vertical transition to the ground state is impossible. The absence of any significant luminescence is therefore immediately explained, as is the presence of the long-lived state detected in photoinduced absorption by Shank *et al.* (1982).

There still remains the question of the short-lived component of the photoinduced absorption, and why this decays; there is of course a significant amount of energy available in the system soon after photoexcitation, and this could raise the exciton's energy up to the crossover, thereby permitting non-radiative decay.

This explanation of the observed luminescence quenching does not remove the need for CCS to be violated, of course, but does allow for the magnitude of the violation to be much smaller than that required by the simple competition model. The decay time can be of the order of some picoseconds, rather than requiring the entire decay to take place in less than 150fs as required by the latter model.

The principal difference between the predictions of the SSH and CNDO models occurs because of the differences in the predicted depths of the defect, i.e. the values of the configuration co-ordinate α at which the excited state energy minimum occurs. It can easily be seen that, if the minimum of the SSH curve is moved out from $\alpha=1.05$ to $\alpha=1.8$ in order to agree with that of CNDO, and if the vibrational frequency is left unaltered, the configuration co-ordinate diagram becomes qualitatively equivalent to that of CNDO, so that the predictions would be changed accordingly.

From this observation, the conclusion can be drawn that the principal reason that the SSH model's predictions concerning the efficiency of luminescence in c-PA are so difficult to reconcile with experiment lies with the method by which the SSH model has been adjusted to deal with polymers without ground state degeneracy. In view of the entirely arbitrary nature of the process that was used to do so, this does not seem surprising; one of the advantages of CNDO is that it makes no such arbitrary assumptions.

It was mentioned in §6.3 that there was one piece of experimental evidence available which supported the predictions of CNDO concerning the defect depth: the photoinduced IR measurements of Tanaka *et al.* (1984), who found evidence of complete reversal of the dimerisation in photoexcited polythiophene. This duplicates the CNDO result and describes a defect nearly twice as deep as that predicted by the SSH model. Apart from this one observation, there is regrettably no direct experimental evidence to test the CNDO predictions.

The results of this chapter can be summarised as follows:

- (i) The SSH model is unable to account for the quenching of luminescence in c-PA, even if charge conjugation symmetry is violated.
- (ii) The results of the CNDO method can explain not only the low efficiency of luminescence, but also the existence of the long-lived defect state observed experimentally.
- (iii) The principal reason for the very different predictions of the two methods is that they predict different depths for the defect-induced distortion. If SSH predicted the same depth as CNDO, the further predictions of CNDO would also be reproduced.
- (iv) The luminescence quenching still requires CCS to be broken. However, the symmetry-breaking does not need to be as strong as is required if the quenching is assumed to be due to a competitive non-radiative process, since cold luminescence is now predicted to be forbidden.

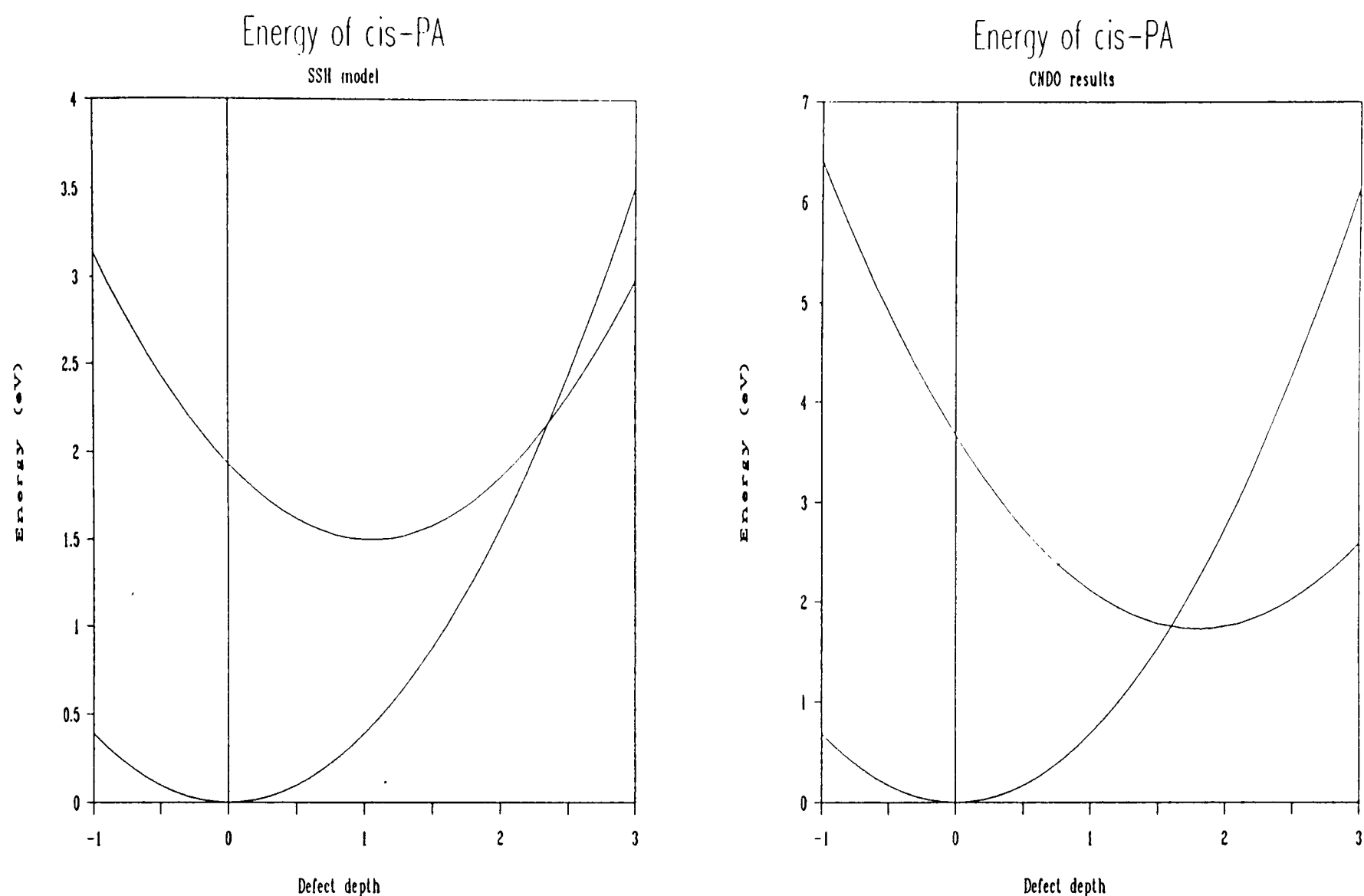


Fig. 7.1 Configuration co-ordinate diagrams for the exciton in c-PA, within the SSH (left hand graph) and CNDO models (see §7.3). In each graph, there is one important point to note. Within the SSH model, the crossover occurs at higher energy than the vertical excitation energy, meaning that a non-radiative decay is expressly forbidden by energy conservation, rather than just by CCS; within CNDO, the energy minimum of the excited state curve lies *outside* the ground state curve, thereby explaining why no cold luminescence is seen and accounting for the observed long-lived defect state.

APPENDIX 1 MATHEMATICAL DERIVATIONS

1.1 CALCULATION OF ANALYTIC COULOMB INTEGRALS OVER SLATER S ORBITALS

The dynamical nature of the relaxation process requires us to calculate not only Coulomb integrals themselves, but also their derivatives with respect to atomic separation R . The method traditionally used for calculation of the integrals, that of expressing them in terms of reduced overlap integrals (Pople & Beveridge 1980, Appendix B.5), is not ideally suited to this, and here we attempt to find a method which gives the integrals in a more easily differentiable form. Roothaan (1951) has given analytic results for principal quantum numbers $n=1$ and $n=2$, but not for higher values of n , and calculation of the integrals and derivatives for general n is desirable. While evaluation by the same method as Roothaan merely requires some straightforward algebraic manipulation, the quantity of this manipulation is sufficient to render the task extremely unattractive and the calculations must be repeated for each pair of principal quantum numbers. Here the general Coulomb integrals are found in a form suitable for implementing in a computer program, and for differentiating as well.

We need the results:

$$A_n(\rho) \equiv \int_1^\infty \xi^n e^{-\rho\xi} d\xi = \frac{n!e^{-\rho}}{\rho^{n+1}} \sum_{k=0}^n \frac{\rho^k}{k!}$$
$$B_n(\rho) \equiv \int_{-1}^1 \eta^n e^{-\rho\eta} d\eta = -A_n(\rho) - (-1)^n A_n(-\rho)$$
$$= \frac{n!}{\rho^{n+1}} \left[e^{\rho} \sum_{k=0}^n \frac{(-1)^k \rho^k}{k!} - e^{-\rho} \sum_{k=0}^n \frac{\rho^k}{k!} \right]$$

and $B_n(-\rho) = (-1)^n B_n(\rho)$.

Two sets of co-ordinates are used: the wave functions are written in terms of r_a , r_b and φ , where r_a and r_b are the distances from a general point to the cores of atoms A and B and φ is the azimuthal angle, while the integrations are carried out using a spheroidal basis set ξ , η and φ . The

two bases are related by:

$$r_a = \frac{1}{2}R(\xi+\eta) \quad r_b = \frac{1}{2}R(\xi-\eta),$$

where R is the interatomic distance, and the limits of integration in the spheroidal basis are that φ is integrated from 0 to 2π , η from -1 to 1 and ξ from 1 to ∞ . The volume element in the spheroidal basis is given by $d\tau = R^3(\xi^2-\eta^2)d\xi d\eta d\varphi/8$.

Recall that the Slater s orbitals are given by:

$$(ns) = \frac{(2\xi)^{n+\frac{1}{2}}}{[(2n)!]^{\frac{1}{2}}} r^{n-1} e^{-\xi r} \cdot \frac{1}{\sqrt{4\pi}}$$

The resultant charge distribution $(ns)^2$ is denoted by Ω .

The first step in the calculation is the evaluation of the potential of electron 2 (for example) due to the charge distribution of electron 1. For s orbitals, Roothaan showed that it was equal to the nuclear attraction integral $\int \chi_b^2/r_a d^3r$, and this is evaluated below.

$$\begin{aligned} \text{Put } U &= \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \cdot \frac{(2\xi)^{2n+1}}{4\pi \cdot (2n)!} \cdot r_b^{2n-2} e^{-2\xi r_b} \cdot \frac{1}{r_a} \cdot \frac{R^3}{8} \cdot (\xi^2 - \eta^2) \\ &= \frac{1}{R} \cdot \frac{\rho^{2n+1}}{(2n)!} \int_{-1}^1 d\eta \int_1^\infty d\xi (\xi - \eta)^{2n-1} e^{-\rho(\xi - \eta)} \end{aligned}$$

where $\rho = \xi R$. Expanding the binomial term, we can express this in terms of A and B integrals as:

$$\begin{aligned} U &= \frac{\rho^{2n+1}}{2nR} \sum_{m=0}^{2n-1} \frac{B_m(\rho) A_{2n-1-m}(\rho)}{m! (2n-1-m)!} \\ &= \frac{1}{2nR} \sum_{m=0}^{2n-1} \sum_{k=0}^m \sum_{j=0}^{2n-1-m} \left[\frac{(-1)^k \rho^{k+j}}{k! j!} - e^{-2\rho} \cdot \frac{\rho^{k+j}}{k! j!} \right] \end{aligned}$$

We can express the summations in terms of $(k+j)$ and k , in which case the summation over m becomes trivial, and we get:

$$U = \frac{1}{2nR} \sum_{(k+j)=0}^{2n-1} (2n - (k+j)) \sum_{k=0}^{k+j} \left[\frac{(-1)^k \rho^{k+j}}{k! (k+j-k)!} - e^{-2\rho} \cdot \frac{\rho^{k+j}}{k! (k+j-k)!} \right]$$

Now $(\rho \pm \rho)^a = \sum_{i=0}^a \frac{(\pm 1)^i \cdot \rho^a \cdot a!}{i! (a-i)!}$, so:

$$U = \frac{1}{R} \left[1 - \frac{e^{-2\rho}}{2n} \sum_{a=0}^{2n-1} (2n-a) \frac{(2\rho)^a}{a!} \right]$$

We can now write down an expression for the Coulomb integral itself:

$$\begin{aligned} \gamma_{AB} &= \int U_A \Omega_B d\tau \\ &= \int_0^{2\pi} d\varphi \int_{-1}^1 d\eta \int_1^\infty d\xi \frac{1}{r_a} \left[1 - \frac{e^{-2\xi_a r_a}}{2n_a} \sum_{m=0}^{2n_a-1} (2n_a-m) \frac{(2\xi_a r_a)^m}{m!} \right] \\ &\quad \frac{(2\xi_b)^{2n_b+1}}{4\pi(2n_b)!} \cdot r_b^{2n_b-2} \cdot e^{-2\xi_b r_b} \cdot \frac{R^3}{8} (\xi^2 - \eta^2) \\ &= \frac{1}{R} \int_{-1}^1 d\eta \int_1^\infty d\xi \left[1 - \frac{e^{-\rho_a(\xi+\eta)}}{2n_a} \sum_{m=0}^{2n_a-1} (2n_a-m) \frac{\rho_a^m}{m!} (\xi+\eta)^m \right] \\ &\quad \frac{\rho_b^{2n_b+1}}{(2n_b)!} \cdot (\xi-\eta)^{2n_b-1} \cdot e^{-\rho_b(\xi-\eta)} \end{aligned}$$

The integration corresponding to the 1 inside the bracket is the same as that performed earlier in calculating U , and will give $1/R$ + terms in $e^{-2\rho_b}$. These will not, however, be the only terms in $e^{-2\rho_b}$; others will come from the more complicated integration. Now if we find either the terms in $e^{-2\rho_a}$ or those in $e^{-2\rho_b}$, we can write down the terms in the other by symmetry. Accordingly, this integral is ignored, and only terms in $e^{-2\rho_a}$ (which all arise from the same source) are considered, those in $e^{-2\rho_b}$ being written down later. Expanding out the binomial terms:

$$\begin{aligned} \gamma_{AB} &= - \frac{1}{R} \sum_{m=0}^{2n_a-1} \frac{(2n_a-m) \rho_a^m \rho_b^{2n_b+1}}{m! (2n_a) (2n_b)!} \cdot \int_{-1}^1 d\eta \int_1^\infty d\xi e^{-(\rho_a+\rho_b)\xi} e^{-(\rho_a-\rho_b)\eta} \\ &\quad \sum_{p=0}^m \frac{m!}{p! (m-p)!} \cdot \xi^p \eta^{1-p} \sum_{q=0}^{2n_b-1} \frac{(2n_b-1)!}{q! (2n_b-1-q)!} \cdot (-1)^{2n_b-1-q} \cdot \xi^q \eta^{2n_b-1-q} \\ &= \frac{1}{R} \sum_{m=0}^{2n_a-1} \frac{(2n_a-m) \rho_a^m \rho_b^{2n_b+1}}{m! (2n_a) (2n_b)!} \cdot \sum_{p=0}^m \frac{m!}{p! (m-p)!} \cdot \sum_{q=0}^{2n_b-1} \frac{(2n_b-1)!}{q! (2n_b-1-q)!} \cdot \\ &\quad (-1)^q A_{p+q}(\rho_a+\rho_b) B_{2n_b+m-1-p-q}(\rho_a-\rho_b) \end{aligned}$$

Now $A_{p+q}(\rho_a + \rho_b) B_{2n_b+m-1-p-q}(\rho_a - \rho_b)$

$$= \frac{(p+q)! e^{-(\rho_a + \rho_b)}}{(\rho_a + \rho_b)^{p+q+1}} \sum_{k=0}^{p+q} \frac{(\rho_a + \rho_b)^k}{k!} \cdot \frac{(2n_b+m-1-p-q)!}{(\rho_a - \rho_b)^{2n_b+m-p-q}} \cdot \left[e^{\rho_a - \rho_b} \sum_{j=0}^J \frac{(-1)^j (\rho_a - \rho_b)^j}{j!} - e^{-(\rho_a - \rho_b)} \sum_{j=0}^J \frac{(\rho_a - \rho_b)^j}{j!} \right]$$

where J has been written for $(2n_b+m-1-p-q)$ in the summation limits. The first term in the bracket will lead to terms in $e^{-2\rho_b}$, and is therefore ignored for the same reason as before. This enables us to define a new quantity γ_{AB}^* , representing the terms in $e^{-2\rho_a}$:

$$\gamma_{AB}^* = - \frac{e^{-2\rho_a}}{R} \sum_{m=0}^{2n_a-1} \sum_{p=0}^m \sum_{q=0}^{2n_b-1} \sum_{k=0}^{p+q} \sum_{j=0}^J \frac{(2n_a-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot \frac{\rho_a^m \rho_b^{2n_b+1} (\rho_a + \rho_b)^k (\rho_a - \rho_b)^j}{(\rho_a + \rho_b)^{p+q+1} (\rho_a - \rho_b)^{2n_b+m-p-q}} \cdot \frac{(p+q)! (2n_b+m-1-p-q)!}{p! (m-p)! q! (2n_b-1-q)! k! j!}$$

The quintuple summation involved is not easily tractable, but, more importantly, the expression is easily differentiable if ρ_a is replaced by $\zeta_a R$ etc.. Expressions for γ_{AB} and its derivative are given, in full, at the end of this appendix.

The calculations above have assumed that $\rho_a \neq \rho_b$, i.e. $\zeta_a \neq \zeta_b$. If the two exponents are equal (which will normally come about when atoms A and B are of the same type), we have a simpler form for the Coulomb integral:

$$\gamma_{AB} = \frac{1}{R} \int_{-1}^1 d\eta \int_1^\infty d\xi \left[1 - \frac{e^{-\rho(\xi+\eta)}}{2n_a} \sum_{m=0}^{2n_a-1} (2n_a-m) \frac{\rho^1}{m!} (\xi+\eta)^m \right] \cdot \frac{\rho^{2n_b+1}}{(2n_b)!} (\xi-\eta)^{2n_b-1} e^{-\rho(\xi-\eta)}$$

Again, the term arising from the 1 inside the bracket has been evaluated earlier; the remainder is calculated by expanding the binomials as before:

$$\gamma_{AB}^* = \frac{1}{R} \int_{-1}^1 d\eta \int_1^\infty d\xi e^{-2\rho\xi} \cdot \frac{1}{2^{n_a}} \sum_{m=0}^{2^{n_a}-1} (2^{n_a}-m) \frac{\rho^1}{m!} \sum_{k=0}^m \xi^k \eta^1 \frac{m!}{k!(m-k)!} \cdot$$

$$\frac{\rho^{2n_b+1}}{(2n_b)!} \sum_{j=0}^{2^{n_b}-1} \xi^j \eta^{2n_b-1-j} (-1)^j \frac{(2n_b-1)!}{j!(2n_b-1-j)!}$$

The crucial difference between this and the more general form, with $\zeta_a \neq \zeta_b$, is that there is no exponential term in η . Instead, the integrand containing η is merely η^a , where a is an integer, and this gives $(1+(-1)^a)/(a+1)$ for the integral. Writing out the A integrals, we therefore get:

$$\gamma_{AB}^* = \frac{e^{-2\rho}}{R} \cdot \frac{1}{4^{n_a n_b}} \sum_{m=0}^{2^{n_a}-1} \sum_{k=0}^m \sum_{j=0}^{2^{n_b}-1} \sum_{p=0}^{k+j} \frac{(2^{n_a}-m)}{2^{n_b+m-j-k}} [(-1)^j - (-1)^{m-k}] \cdot$$

$$\frac{(k+j)!}{k!j!} \cdot \frac{1}{(m-k)!(2n_b-1-j)!} \cdot \frac{1}{p!} \cdot \frac{1}{2^{k+j+1-p}} \cdot \rho^{2n_b+m+p-k-j}$$

And to this we can add the term we omitted earlier. The resulting expressions are also given below, and have been verified against Roothaan's formulae by directly enumerating the terms of the summation for $n_a=n_b=1$. The integrals all tend asymptotically to $1/R$ for large R ; graphs of two sample integrals and their derivatives are shown in figs. A1.1 and A1.2 respectively.

1. General case: $\zeta_a \neq \zeta_b$

$$\gamma_{AB} = 1/R$$

$$\begin{aligned}
& - e^{-2\zeta_a R} \sum_{m=0}^{2n_a-1} \sum_{p=0}^m \sum_{q=0}^{2n_b-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_b} \frac{(2n_a-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot R^{k+j-1} \\
& \quad \zeta_a^m \zeta_b^{2n_b+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_a - \zeta_b)^{j-2n_b-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_b+m-1-p-q)!}{p!(m-p)!q!(2n_b-1-q)!k!j!} \\
& - e^{-2\zeta_b R} \sum_{m=0}^{2n_b-1} \sum_{p=0}^m \sum_{q=0}^{2n_a-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_a} \frac{(2n_b-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot R^{k+j-1} \\
& \quad \zeta_b^m \zeta_a^{2n_a+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_b - \zeta_a)^{j-2n_a-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_a+m-1-p-q)!}{p!(m-p)!q!(2n_a-1-q)!k!j!}
\end{aligned}$$

where $J_{a,b}$ have been written for $(2n_{a,b}+m-1-p-q)$ in the summation limits (as below).

$$\frac{\partial \gamma_{AB}}{\partial R} = -1/R^2$$

$$\begin{aligned}
& - e^{-2\zeta_a R} \sum_{m=0}^{2n_a-1} \sum_{p=0}^m \sum_{q=0}^{2n_b-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_b} \frac{(2n_a-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot \\
& \quad \zeta_a^m \zeta_b^{2n_b+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_a - \zeta_b)^{j-2n_b-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_b+m-1-p-q)!}{p!(m-p)!q!(2n_b-1-q)!k!j!} \cdot [(k+j-1)R^{k+j-2} - 2\zeta_a R^{k+j-1}] \\
& - e^{-2\zeta_b R} \sum_{m=0}^{2n_b-1} \sum_{p=0}^m \sum_{q=0}^{2n_a-1} \sum_{k=0}^{p+q} \sum_{j=0}^{J_a} \frac{(2n_b-m)}{2n_a \cdot 2n_b} \cdot (-1)^q \cdot \\
& \quad \zeta_b^m \zeta_a^{2n_a+1} (\zeta_a + \zeta_b)^{k-p-q-1} (\zeta_b - \zeta_a)^{j-2n_a-m+p+q} \cdot \\
& \quad \frac{(p+q)!(2n_a+m-1-p-q)!}{p!(m-p)!q!(2n_a-1-q)!k!j!} \cdot [(k+j-1)R^{k+j-2} - 2\zeta_b R^{k+j-1}]
\end{aligned}$$

2. Special case: $\zeta_a = \zeta_b$

$$\gamma_{AB} = 1/R$$

$$+ e^{-2\zeta R} \cdot \frac{1}{4n_a n_b} \sum_{m=0}^{2n_a-1} \sum_{k=0}^m \sum_{j=0}^{2n_b-1} \sum_{p=0}^{k+j} \frac{(2n_a-m)}{2n_b+m-j-k} [(-1)^j - (-1)^{m-k}] \cdot \frac{(k+j)! \zeta^{2n_b+m+p-k-j}}{k! j! (m-k)! (2n_b-1-j)! p! 2^{k+j+1-p}} \cdot R^{2n_b+m+p-k-j-1} \\ - \frac{e^{-2\zeta R}}{2n_b} \sum_{a=0}^{2n_b-1} (2n_b-a) \frac{(2\zeta)^a R^{a-1}}{a!}$$

$$\frac{\partial \gamma_{AB}}{\partial R} = -1/R^2$$

$$+ e^{-2\zeta R} \cdot \frac{1}{4n_a n_b} \sum_{m=0}^{2n_a-1} \sum_{k=0}^m \sum_{j=0}^{2n_b-1} \sum_{p=0}^{k+j} \frac{(2n_a-m)}{2n_b+m-j-k} [(-1)^j - (-1)^{m-k}] \cdot \frac{(k+j)! \zeta^{2n_b+m+p-k-j}}{k! j! (m-k)! (2n_b-1-j)! p! 2^{k+j+1-p}} \cdot \\ [(2n_b+m+p-k-j-1) R^{2n_b+m+p-k-j-2} - 2\zeta R^{2n_b+m+p-k-j-1}] \\ - \frac{e^{-2\zeta R}}{2n_b} \sum_{a=0}^{2n_b-1} (2n_b-a) \frac{(2\zeta)^a}{a!} [(a-1) R^{a-2} - 2\zeta R^{a-1}]$$

1.2 CALCULATION OF THEORETICAL HUANG-RHYS FACTORS IN POLYACETYLENE

It appears, from self-consistent model calculations, that the modes which are displaced on photoexcitation of either of the polyacetylene isomers are principally the vibrational modes of the carbon chain, and so here we assume that these are the only modes that we need to consider for this purpose, i.e. that a 1-D approximation is valid. We start by assuming a displacement pattern of the form:

$$u(x) = u_0 - p \{ \tanh[(x-x_1)/\ell] - \tanh[(x-x_2)/\ell] \}$$

which is an exact solution in the SSH model, and a good approximation to that obtained using CNDO. It applies, to a reasonable approximation, to both PA isomers, although the constants may not be the same in each case. A factor $(-1)^n$, i.e. $e^{ix\pi/a}$, has been omitted, since this just moves the

origin in k-space to π/a , i.e. to $k=0$ in the optic band. Subtracting the constant term, which represents the ground state solution, and expressing this displacement in k-space, we get:

$$u(k) \approx N^{-\frac{1}{2}} \int_{L/2}^{L/2} u(x) e^{ikx} (dx/a)$$

$$\approx \frac{p}{\sqrt{La}} \int_{-\infty}^{\infty} \{ \tanh[(x-x_1)/\ell] - \tanh[(x-x_2)/\ell] \} e^{ikx} dx$$

If we make the substitutions $z=[2x-(x_1+x_2)]/2\ell$ and $z_0=(x_1-x_2)/2\ell$, this becomes:

$$u(k) \approx \frac{p}{\sqrt{La}} \int_{-\infty}^{\infty} \frac{-\sinh(2z_0)}{\cosh(z-z_0)\cosh(z+z_0)} e^{ik\ell z} e^{ik(x_1+x_2)/2} \ell dz$$

$$\approx \frac{-2p}{\sqrt{La}} \int_{-\infty}^{\infty} \frac{\sinh(2z_0)}{\cosh(2z) + \cosh(2z_0)} e^{ik\ell z} e^{ik(x_1+x_2)/2} \ell dz$$

where the hyperbolic functions have been manipulated into a more easily integrable form (Abramovitz & Stegun 1985, p.84).

Returning to our original scale (but with the origin shifted to the mid-point of the polaron) by putting $x=\ell z$, we get:

$$u(k) \approx -4 \sinh(2z_0) e^{ik(x_1+x_2)/2} \int_{-\infty}^{\infty} [\cosh(2x/\ell) + \cosh(2z_0)]^{-1} \cos kx dx$$

and, by writing $\cosh(2iz_0)$ for $\cosh(2z_0)$, we obtain an integral which appears in the standard works (e.g. Erdelyi *et.al.* 1954, p.30). The result is:

$$u(k) \approx \frac{2\pi\ell p}{\sqrt{La}} \sin[k(x_2-x_1)/2] \operatorname{cosech}(k\ell\pi/2) \quad (|x_2-x_1| < \pi\ell)$$

giving the Huang-Rhys factor, at zero temperature:

$$S_{0k} \approx \frac{2M_k\omega_k\pi^2\ell^2p^2}{hLa} \sin^2[k(x_2-x_1)/2] \operatorname{cosech}^2(k\ell\pi/2) \quad (A1.1)$$

Plots of $\ell^2 \sin^2[k(x_2-x_1)/2] \operatorname{cosech}^2(k\ell\pi/2)$ against k , for various values of ℓ and (x_2-x_1) (fig. A1.3), show that the Huang-Rhys factors are very small for k greater than approximately $0.1\pi/a$. Over this range, the dispersion of the optic phonons is only of the order of 10% (see fig. 3.3),

and can be ignored to a fairly good approximation, allowing us to calculate a total Huang-Rhys factor:

$$S_0 \approx \int_{-\infty}^{\infty} S_{0k} (L/2\pi) dk$$

$$S_0 \approx - \frac{M\omega\ell^2 p^2}{\hbar a} \int_{-\infty}^{\infty} \frac{\sinh^2[ik(x_2-x_1)/2]}{\sinh^2(k\ell\pi/2)} dk$$

where we have written the numerator in this form to obtain another standard integral (Gradshteyn & Ryzhik 1965, p.344). Evaluation of this integral gives:

$$S_0 \approx \frac{2M\omega\ell^2 p^2}{\hbar a} \left[\left[\frac{x_2-x_1}{\ell} \right] \coth \left[\frac{x_2-x_1}{\ell} \right] - 1 \right]$$

Note that the maximum displacement from the ground state geometry is not p , but $2p \cdot \tanh[(x_2-x_1)/2\ell]$; if we call this $u_{\max}$, and put $u_{\max} = \alpha u_0$, we get:

$$S_0 \approx \frac{M\omega\ell^2 \alpha^2 u_0^2}{2\hbar a} \coth^2 \left[\frac{x_2-x_1}{2\ell} \right] \left[\left[\frac{x_2-x_1}{\ell} \right] \coth \left[\frac{x_2-x_1}{\ell} \right] - 1 \right]$$

Using the observed Raman frequency of 1540cm^{-1} for c-PA (Lefrant *et al.* 1979), this gives:

$$S_0 \approx 0.18 (\ell/a) \alpha^2 G[(x_2-x_1)/\ell] \quad (\text{A1.2})$$

where:

$$G(x) \equiv \coth^2(x/2) [x \coth x - 1].$$

Now G is a fairly slowly varying function (fig. A1.4); over the range of interest, which is something like $1.3 < x < 3.0$, it varies by a factor of only about 1.6, so the Huang-Rhys factor depends more on the width of each tanh function than on the separation between them. This seems surprising at first sight, but is explained by the fact that much of the dependence on the separation is implicitly included within the amplitude α .

To find a typical value of S_0 , consider the case $(x_2-x_1)=9$, $\ell=7$. Then $G=1.6$ and $S_0 \approx 2\alpha^2$. Specific examples will be considered in the text.

1.3 DAMPING OF THE ATOMIC MOTION

Finding the minimum energy geometry of a system by a molecular dynamical

method is strongly dependent for its efficiency on suitable choices of the time step and damping factor. It is intuitively obvious that the time step has to be of order $1/\omega$, where ω is the angular velocity of the normal mode whose vibrations are being "frozen out" of the system, but how to optimise the choice of parameters when more than one normal mode has to be considered is not immediately obvious, and a brief mathematical analysis is presented here.

The iterative process for atomic relaxation leads to the following equation:

$$X(t+h) = -\frac{h^2}{M} \frac{\partial^2 E}{\partial X^2} + (1+\xi)X(t) - \xi X(t-h)$$

If we assume, for simplicity, that we are dealing with one normal mode only, with equilibrium displacement zero, and that the time step used is sufficiently small that the Fock matrix remains close to its self-consistent value throughout the minimisation process (which is essentially the Born-Oppenheimer approximation), this becomes (with the obvious notation $X_n \equiv X(t)$ etc.):

$$X_{n+1} = (1+\xi-h^2\omega^2)X_n - \xi X_{n-1}$$

Writing $\alpha=h\omega$, this has the solution (for $\alpha \neq 1-\sqrt{\xi}$, which represents critical damping):

$$X_n = Pa_1^n + Qa_2^n$$

where a_1 and a_2 are the solutions to the indicial equation and are given by:

$$2a = (1+\xi-\alpha^2) \pm \sqrt{[(1-\alpha)^2-\xi][(1+\alpha)^2-\xi]} \quad (A1.3)$$

For $\alpha = 1-\sqrt{\xi}$, the solution is $X_n = (P+Qn)a^n$, of course.

Except in extremely unusual circumstances, the larger (in magnitude) of these solutions will dominate in the relaxation process. The dependence of the solutions on α (and hence on the time step) is outlined here.

For small α , the larger root is approximately $1-\alpha^2/(1-\xi)$, so convergence is improved by reducing the applied damping. This root becomes smaller, and the other root increases, until they meet at the critical damping point

$\alpha=1-\sqrt{\xi}$, when $a=\sqrt{\xi}$. For $1-\sqrt{\xi} < \alpha < 1+\sqrt{\xi}$, the roots are complex conjugates, with constant magnitude $\sqrt{\xi}$ and phase moving from 0 to $\pm\pi$ (so the mode will decay in some oscillatory fashion, as a real linear combination of these two solutions). At $\alpha=1+\sqrt{\xi}$, the roots become real again, this time both negative, and as α becomes large, the larger root (in magnitude) tends to $1+\xi-\alpha^2$. There are no stationary values of a . The absolute upper limit of α for which relaxation can take place is $\sqrt{2(1+\xi)}$, above which $a < -1$; this is the only possible means by which instability can be generated.

A graph of $|a|$ against α , plotted for a range of damping factors in Fig. A1.5, shows how an increase in ξ reduces the maximum speed of relaxation, but increases the range of frequencies over which relaxation can effectively take place. Finding optimal values of ξ and h , therefore, involves a trade-off between these two considerations; what is important is the frequency range over which we expect to observe (and hence to have to "freeze out") normal modes.

If we expect modes with angular velocities between $\omega_{\min}$ and $\omega_{\max}$ ($=R\omega_{\min}$), we can obtain minimisation at constant speed by choosing $\xi = [(R-1)/(R+1)]^2$, $h = 2/(\omega_{\min}+\omega_{\max})$; the amount of each normal mode will be reduced by a factor $\sqrt{\xi}$ at each step.

A typical range of frequencies which we may need to consider might be the range 500cm^{-1} to 5000cm^{-1} (recall that values calculated by CNDO tend to be 50-60% higher than experimentally observed, so the C-H bond stretch typically observed at around 3300cm^{-1} (Williams and Fleming 1980) should occur at about 5000cm^{-1} in CNDO; stretching modes involving hydrogen will normally be the highest frequency modes that need to be considered, although it may be possible that ionic or strongly polar systems could exhibit modes of even higher frequency). The natural units of the calculation correspond are such that $\omega=1$ represents a frequency of approximately 5120cm^{-1} , so to optimise the speed of convergence throughout this range we could choose $\xi=0.65$, $h=1.8$. In this case the amount of each

normal mode present should decay by about 20% on each step, corresponding to a requirement of ≈ 10 steps for each extra significant figure required in the relaxed geometry (i.e. if the initial geometry is accurate to 1 d.p., it will take about 10 steps to reach a geometry accurate to 2 d.p. and about 20 for a geometry accurate to 3 d.p.). It will be safer, if in doubt about the range of frequencies to be considered, to overdamp the system (with, say, $\xi=0.5$, $h=1.0$) than to underdamp, the more so because of the non-linearity that may be encountered at large distortions and the possibility of violating the Born-Oppenheimer approximation; overdamping can never lead to instability, while underdamping can.

The advantages to be had by careful choice of ξ and h can be seen if we consider the geometry optimisation of methane. We start (for the sake of this example) from an asymmetric state, where the initial modes present are essentially the H-C-H bend observed at 1306cm^{-1} and the C-H symmetric stretch observed at 2914cm^{-1} (Herzberg 1945). Consider three pairs of damping parameters: $\xi=0$, $h=1$ (designed to "freeze out" the C-H mode as quickly as possible, with no regard to the bending mode), $\xi=0.25$, $h=1.5$ (designed to optimise convergence for $\omega \approx 0.3$ to 1.0 , i.e. specifically chosen for this molecule) and $\xi=0.65$, $h=1.8$ (the all-purpose values above). The behaviours of a typical C-H bond length and one of the distorted H-C-H bond angles are shown in Fig. A1.6 and A1.7 respectively: The first pair, as predicted, finds the equilibrium bond length very quickly indeed, but convergence is slow as far as the angle is concerned; the all-purpose pair leads to moderately good convergence for both, but the pair chosen specifically for methane is clearly the best of the three, converging well in within 10 steps or so (the atoms were held fixed for 3 steps, to allow the Fock matrix time to reach a reasonable approximation).

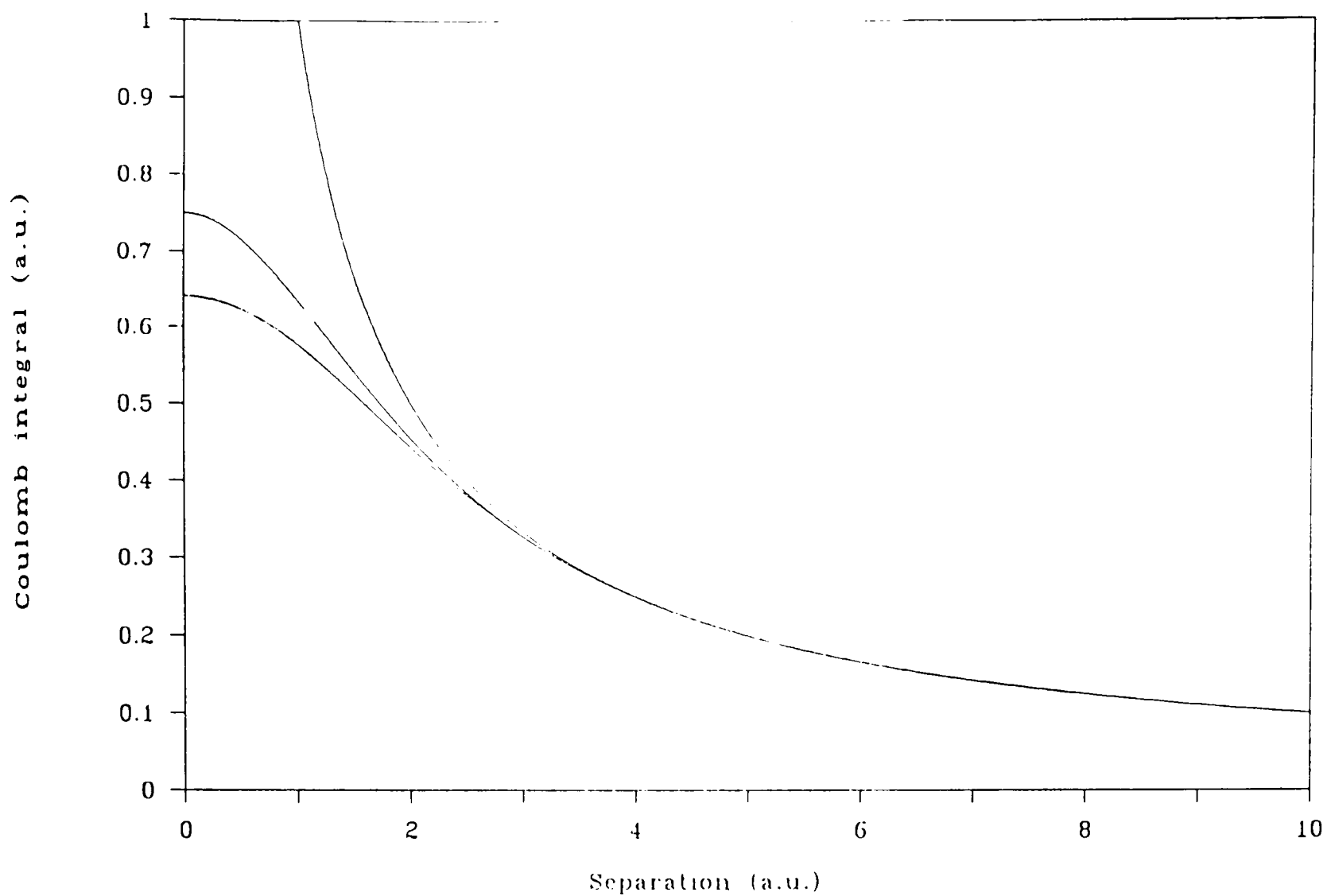


Fig. A1.1 Coulomb integral $\gamma_{AB}(R)$ against atomic separation R for cases (1) γ_{HH} (2) γ_{CN} . The third curve is the long-distance limit $\gamma = 1/R$.

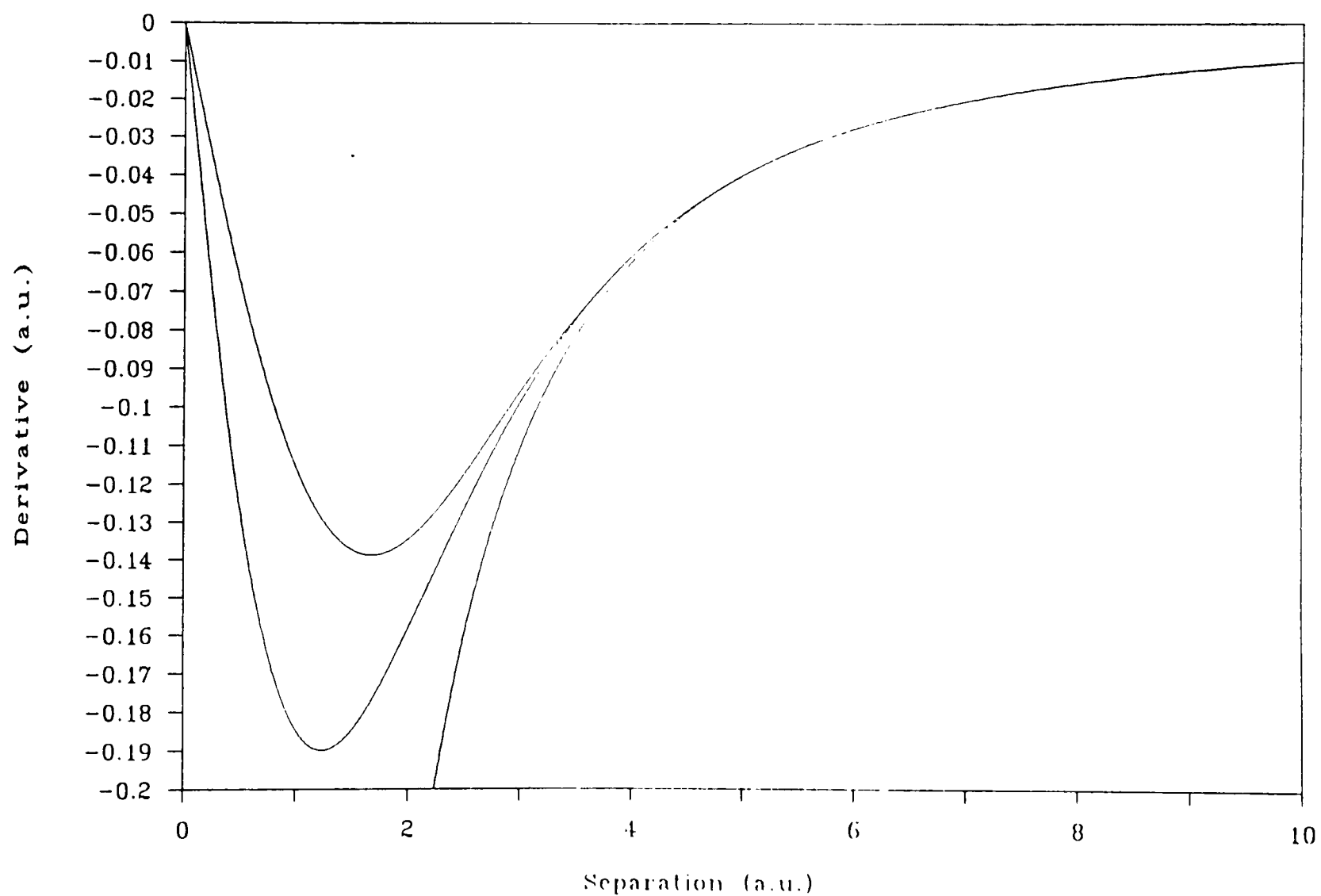


Fig. A1.2 Derivatives of the Coulomb integral for the same cases as fig. A1.1.

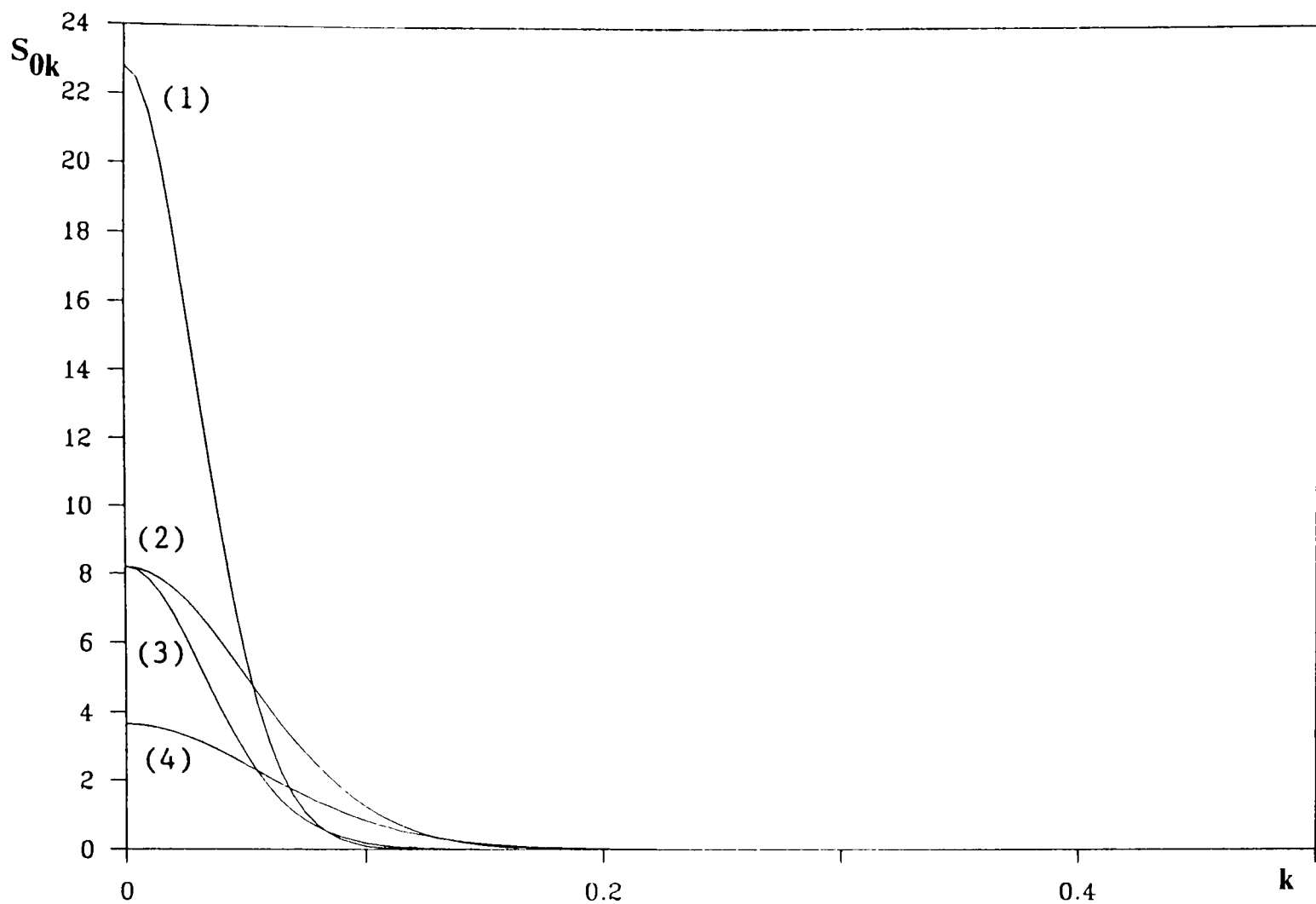


Fig. A1.3 Huang-Rhys factor S_{0k} (arbitrary units) against k (in units of π/a) for a polaron in four cases: (1) $x_2 - x_1 = 15$, $\ell = 7$ (2) $x_2 - x_1 = 9$, $\ell = 4$ (3) $x_2 - x_1 = 9$, $\ell = 7$ (4) $x_2 - x_1 = 6$, $\ell = 4$. Note that the factors (given by (A1.1) on p. A1.8) are only significant for k less than about $0.1\pi/a$, over which range the optic band phonon dispersion relation (fig. 3.3) is extremely flat.

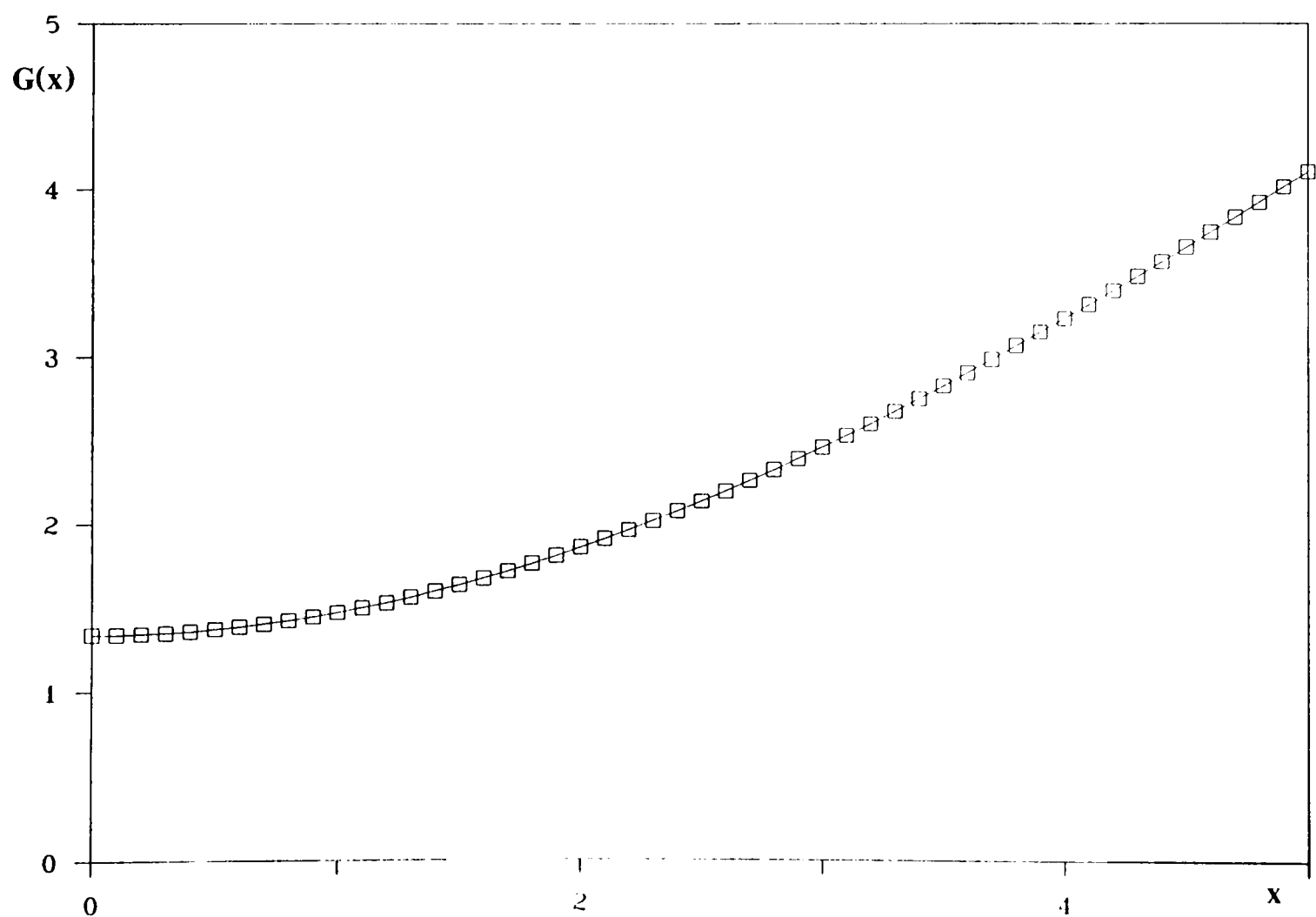


Fig. A1.4 Geometrical factor $G(x)$ against x (see (A1.2), p. A1.9).

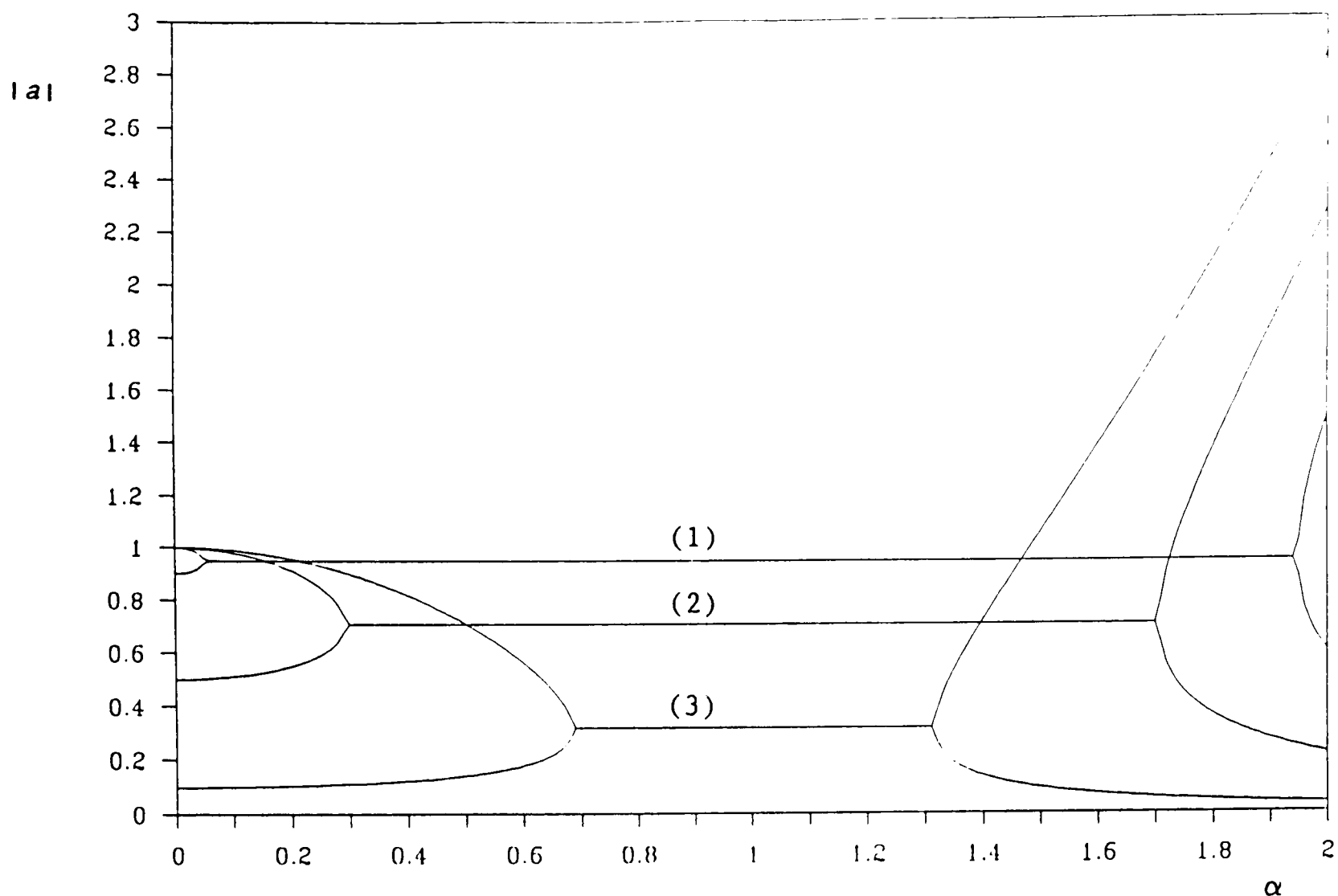


Fig. A1.5 Rate of decay of normal mode amplitude, against effective time step α ($=h\omega$) (see (A1.3), p. A1.10). Damping parameters (1) $\xi=0.9$ (2) $\xi=0.5$ (3) $\xi=0.1$.

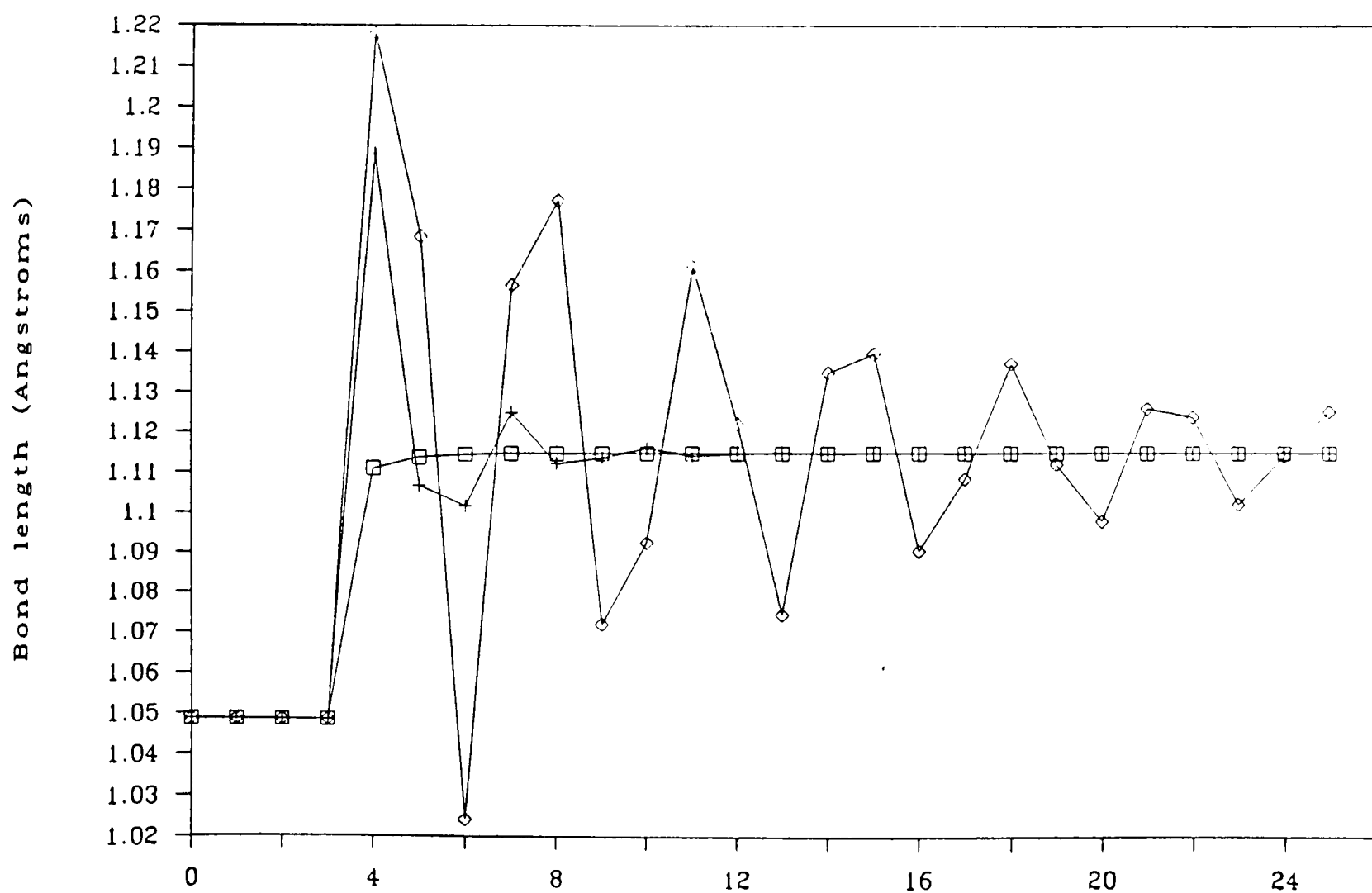


Fig. A1.6 Change in C-H bond length in methane throughout a relaxation run. Parameters used: $\square \xi=0, h=1$ $+ \xi=0.25, h=1.5$ $\diamond \xi=0.65, h=1.5$.

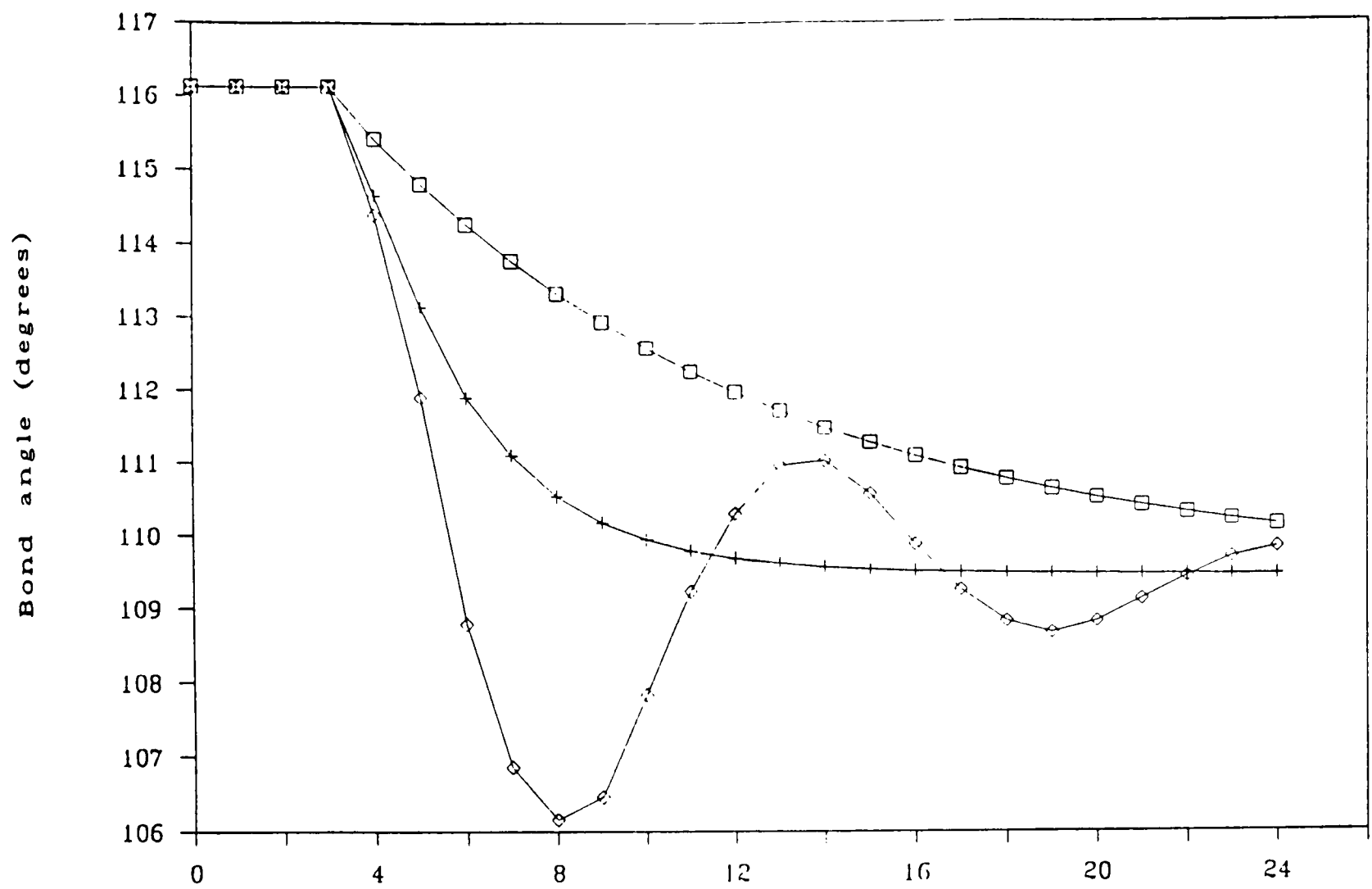


Fig. A1.7 Change in H-C-H bond angle in methane throughout a relaxation run. Same parameters as in fig. A1.6.

INTRODUCTION

Self-consistent ground states are calculated within the CNDO/2 and INDO approximations, using a molecular dynamical method to relax the atomic positions and concurrent matrix diagonalisation to calculate LCAO wave functions based on these positions.

The Fock matrices (and hence the wave functions) are not calculated self-consistently at each geometry encountered along the minimisation path, but at each step of the minimisation process the Fock matrix is diagonalised just once (self-consistency requires repeated diagonalisation). Because of the method used for atomic relaxation, however, the wave functions are expected to represent a good approximation to the self-consistent solutions at the end of the process (since a system moving under dynamical equations of motion towards a minimum will spend most time close to the minimum energy geometry, thereby allowing the wave function diagonalisation to reach approximate self-consistency).

PROGRAM ORIGINS: the routines used come from one of three sources:

- (1) Pople & Beveridge (1970). Those parts of the program which could be taken over from the static case were, in the main, copied directly from the FORTRAN-IV program supplied by these authors, some being translated into FORTRAN-77 in the process.
- (2) MOSES (Harker & Lyon 1979). The routines to calculate overlap integrals were copied from MOSES, itself based on the program of Pople and Beveridge. Acknowledgements are due to A.H.Harker for permission to do so. An outline routine to calculate the dipole matrix element between two atomic orbitals was taken from an updated version of MOSES, with acknowledgements to A.J.Fisher.
- (3) The remaining routines were written specifically for this program, including a routine which calculates Coulomb integrals in analytic

form by a method similar to that of Roothaan (1951), and an input routine allowing for the added flexibility of the geometry optimisation program.

IMPLEMENTATION: The program has been implemented on an IBM PC and an IBM 3084 mainframe computer; the latter version can also be run on the CRAY-2 at Harwell. The PC version is limited to 26 atoms or 65 basis functions, while the mainframe version is currently limited to 100 atoms or 300 basis functions. The low ratio of basis orbitals to atoms is a consequence of the program being designed for the study of conjugated polymers, which have a high proportion of hydrogen atoms. At present, the program can only handle s and p orbitals, which are all that is required for an approximate treatment of conjugated polymers (where the presence of d orbitals, even in atoms with principal quantum number $n=3$, is not expected to make a major contribution to the molecular behaviour), but extension to d orbitals should not present any major difficulty.

APPLICATION TO DYNAMICAL STUDIES: Although the program was originally designed as a means of finding ground states, its molecular dynamical basis means that it can equally be applied to the study of dynamics, with the obvious caveat that the time step used must remain sufficiently small that the atomic motion is not sufficient to pull the Fock matrix away from self-consistency faster than the diagonalisation process can push it towards the self-consistent solution at the given geometry. We could treat the effective electron mass as some (increasing) function of the time step, and this constraint is then equivalent to the requirement that this effective mass remain small.

It is also necessary, when considering the study of dynamical properties (e.g. normal mode frequencies) by this method, to remark that CNDO tends to over-predict force constants by a factor of approximately 2-3, and thus that vibrational frequencies may well be in error by something like 50-70%.

This is not so severe a problem as it seems, however: the over-prediction is so regular as to be almost systematic, and thus the nature of the normal modes calculated may well be quite a good approximation to their true nature; the predicted frequencies can be scaled down in order to obtain improved estimates.

CNDO and INDO, of course, have had good success in predicting molecular geometries (certainly in the prediction of bond lengths and angles), and the ground state calculations are expected to be quite accurate.

EXTENSIONS: Routines are included which enable the user to impose external fields and constraints on the molecule under consideration while still being able to perform the self-consistent geometry optimisation.

The dipole matrix elements between one-electron states can also be calculated at the end of a run; the energy calculated for the transition is the virtual orbital (VO) energy $\Delta E = \epsilon_f - \epsilon_i - J_{fi}$, where J_{fi} is the Coulomb integral between the initial and final states $|i\rangle$ and $|f\rangle$ and $\{\epsilon_i\}$ are the one-electron eigenvalues. It should be noted, however, that the virtual orbital method of calculating transition energies is rarely very accurate.

INPUT REQUIRED

Data are input in "keyword" form, as in a number of quantum chemical programs, in order to maximise the ease of use of the program. Only the number of atoms, the charge and multiplicity and the starting geometry, need be specified. There are eighteen keywords in all, and details of their associated input are given below. All keywords may be abbreviated to their first three letters if desired. Numeric associated input is read in free format.

(1) TITLE

Associated input: one line of up to 72 characters.

This is output at the start of the run, and used solely for identification.

(2) CNDO

Associated input: none.

The CNDO/2 parametrisation will be used (*default*).

(3) INDO

Associated input: none.

The INDO parametrisation will be used.

(4) NUMBERS

Associated input: one line of three integers, specifying (respectively) the total number of atoms in a system, and the charge and spin multiplicity of the system.

This keyword is *mandatory*, and must precede GEOMETRY.

(5) GEOMETRY

Associated input: one line for each atom, consisting of one integer (the atomic number) and three real numbers (the initial x, y and z co-ordinates).

This keyword is *mandatory*.

(6) PRINT

Associated input: one line of six integers. These control the level of printout required; each integer controls the printing of one matrix, and is zero to suppress (*default*) or non-zero to print the relevant matrix. The matrices are:

Bond order matrix - printed at the end of the run only.

Total density matrix - printed at the end of the run only.

Spin density matrix - printed at the end of the run only.

Core Hamiltonian matrix - printed at each step.

Fock matrix - printed at each step.

Eigenvector matrix - printed at the end of the run only.

Where appropriate, both spin-up and spin-down matrices are printed.

(7) DAMPING

Associated input: One line of two real numbers. The first specifies the factor used to damp the atomic motion, the second the time step (in the natural units of the program, where the natural unit of time is m_p atomic units, or approximately 1.05fs). The default is not to perform any geometry minimisation, i.e. to use a zero time step; good all-purpose values are 0.5 and 1.0 respectively.

(8) LIMITS

Associated input: One line of three real numbers and two integers. The first two reals dictate the level of convergence required; if the change in total energy in one step is greater than the first (in eV, default 10^{-5}) or the change in any atomic co-ordinate is greater than the second (in Å, default 10^{-4}) the minimisation process will continue. The third real is the limit of interatomic distance (in Å, default 5.0) beyond which all overlap integrals will be ignored. The two integers specify the number of Fock matrix diagonalisations (default 3) before the atomic relaxation process is to start (this avoids moving the atoms according to forces generated by a wildly inaccurate Fock matrix) and the maximum number of steps (default 25) in the minimisation procedure.

(9) ANGSTROMS

Associated input: none.

The atomic co-ordinates are input in angstrom units (*default*).

(10) ATOMIC

Associated input: none.

The atomic co-ordinates are input in atomic units.

(11) FORCES

Associated input: one line of one integer nf , then nf lines of one integer and three real numbers. The integer nf is the number of atoms subject to the action of external forces, and each line represents one force. The integer is the number of the atom on which the force acts, and the three reals are the three components of the force, in atomic units; $1\text{a.u.} = 8.24 \times 10^{-8}\text{N}$.

(12) HFIX

Associated input: none.

Indicates that hydrogen atoms are to be treated as rigidly attached to their host atoms, with no independent motion allowed.

(13) FIELD

Associated input: One line of three real numbers, representing the x , y and z co-ordinates of a uniform electric field applied to the system. Atomic units are used; $1\text{a.u.} = 5.14 \times 10^{11}\text{Vm}^{-1}$.

(14) XFIELD

Associated input: none.

Indicates that a non-uniform electric field is to be applied, with details in the (user-supplied) subroutine EFIELD.

(15) EXTERNAL

Associated input: none.

Indicates that a force field is to be applied, with details in the (user-supplied) subroutine EXT.

(16) CONSTRAINTS

Associated input: one line of one integer nc , then nc lines of four integers each. The integer nc is the number of atoms whose motion is constrained in some way, and the following lines consist of the number of the atom to be constrained, and three integers controlling the atomic motion in the x , y and z directions respectively. If one of these is zero, motion in the

corresponding direction is forbidden; if non-zero, motion is allowed.

(17) DIPOLE

Associated input: none immediately following the keyword, but at the end of the input deck (i.e. *after* keyword END), two sets of data, specifying the matrix elements required for spin up and spin down states respectively. Each set consists of one line of one integer *nd*, and *nd* lines of three integers. The integer *nd* is the number of calculations to be performed for this spin state, and on each subsequent line the three numbers that serve to specify each calculation are given. These are respectively the numbers of the two molecular orbitals between which the dipole matrix element is required (states are numbered within the program in order of increasing energy), and a number representing the co-ordinate (1≡x, 2≡y, 3≡z). If the second integer, labelling the higher state, is zero, matrix elements will be calculated between the state specified by the first integer and all unoccupied higher states.

(18) END

Associated input: none.

Signals the end of initial input to the program. Only input associated with keyword DIPOLE should follow this keyword.

This keyword is *mandatory*.

PROGRAM STRUCTURE

The program consists of a main program, a BLOCK DATA subprogram and twenty-three subroutines. Of the latter, SS, AINTGS, BINTGS, ERROR, RAISE, FACT and COEFFT were copied from MOSES, and deal with the calculation of reduced overlap integrals. EIGOUT, OPRINT and SCFOUT control the output, and were copied from the program of Pople and Beveridge, modified slightly

to increase their flexibility. EIGN, HARMTR and RELVEC have also been copied from this source; they handle respectively the matrix diagonalisation, the co-ordinate rotation involved in overlap integral calculation and the calculation of a unit vector in the direction joining two atoms (used in HARMTR). Subroutine HUCKOP has been modified slightly, but is very close to the version of Pople and Beveridge; it calculates the core Hamiltonian matrix, used in the calculation of the Fock matrix. Subroutines DIPOLE, ATPAIR, SINGLE and INTGRS have been modified from the MINDO versions of MOSES, and set up the dipole matrices between atomic orbitals.

The remainder of the program has essentially been written especially for this program. The main program handles the input routine above, while subroutine SCFOPN handles the minimisation process, given the necessary first derivatives. These are calculated in INTGRL; the derivatives of the Coulomb integrals are calculated via a call to COUL2 (the original subroutine COULOMB calculated Coulomb integrals and their derivatives in closed form, but only for principal quantum numbers 1 and 2, and has now been replaced by COUL2, which calculates the integrals as summations for any principal quantum number. COULOMB still appears in the code, but is not called), while the derivatives of the overlap integrals are calculated by differentiating the basis orbitals in DPHI. OPTIC calculates dipole matrix elements between molecular orbitals for spin up and spin down.

COMMON BLOCKS

The original program of Pople and Beveridge was written at a time when computer memory was expensive, and therefore makes maximum use of the memory available. It was built about one large common block ARRAYS, containing three NxN arrays (where N is the number of orbitals allowed). Both these arrays, and those that appear in other common blocks, are repeatedly reused for different purposes, and thus modification of the

original program is not a simple task. This new program has been written in such a manner that alteration (e.g. by increasing the number of orbitals allowed) is a trivial process, by reducing the frequency of reuse and by eliminating entirely the process of changing array sizes within a common block. The common blocks in the program consist of four types:

ARRAYS, INFO, GAB, INFO1, DIFFS, DIAGS and ENERGY contain (changing) information about the system, such as the eigenvectors, Fock matrix etc..

PERTBL, ORB, BETAS and XORB are fixed, containing such things as the orbital exponents for each atom type and the labels used in the output.

OPTION, IPRINT, DAMP, LIMITS and FORCES contain details of the input options (OPTION has been renamed OPTIONS in the PC version, due to a requirement of the compiler).

ARR2 is an array used by the overlap integral routines.

USER-SUPPLIED SUBROUTINES

If keywords XFIELD or EXTERNAL have been specified, it is necessary for the user to supply details of the fields they represent in subroutines called EFIELD or EXT respectively. For simplicity, input to, and output from, the subroutines, take the same form in each case. The subroutines should start:

```
SUBROUTINE EXT(X,Y,Z,F,E)
```

```
IMPLICIT REAL*8(A-H,P-Z)
```

```
REAL*8 F(3)
```

The subroutines should return the three components of the appropriate field (electric or force) in F, and the energy in E, calculated in terms of x, y and z co-ordinates sent by the calling program as X, Y and Z.

INPUT/OUTPUT CHANNELS

Input is read from channel 2 in all cases, and output is written to channel 1. When using the IBM mainframe, it is necessary to allocate the

relevant data sets to these channels before running the program (and the data sets must both exist). The most simple method of controlling input/output on the CRAY-2 is to rename the input file as FORT.2; output will be sent to a file FORT.1 (which will be created if necessary) and this in turn can be renamed at the end of the calculation if so desired. On the IBM PC, the user is prompted for input and output file names at the start of the calculation (here, too, the output file will be created if necessary).

PROGRAM ALTERATION

To increase (or decrease) the number of atoms and/or orbitals with which the program can cope, it is only necessary to alter various PARAMETER statements. The maximum numbers of atoms and orbitals allowed are denoted by NATMAX and NORBMX respectively, and all the relevant arrays are dimensioned in terms of these. It is a simple matter to change the PARAMETER statements to incorporate the desired values.

Atomic number 2 has been re-defined as deuterium (in view of the molecular dynamical nature of the code, it was felt that this would be more useful than helium), and the changes that have been made to the code in order to do this are labelled in the code with a message to this effect.

The total amount of memory required by the program is roughly $100K + 72N^2$ bytes - this could in principle be halved by using single precision variables, however. The time-limiting step, at least for large systems, is the matrix diagonalisation, which is why the process is not carried out to self-consistency at each step. No routine which diagonalises matrices faster than $O(N^3)$ is currently available at Harwell; should one become available, it would clearly be advantageous to replace subroutine EIGN by a subroutine which took advantage of this. Details of the format required by EIGN appear, as comment cards, at the start of the subroutine.

The approximate time taken for the CRAY-2 to perform calculations on three

sample molecules is given below, for reference. Note that the increase in going from C₃₄H₂₀ to C₄₈H₅₀ is almost that that would be predicted by an N³ dependence, but the increase between serotonin (C₁₀N₂OH₁₂) and C₃₄H₂₀ (which is a polydiacetylene analogue) is much less.

	Atoms	Basis orbitals	Time per step (s) .
serotonin	25	64	1
C ₃₄ H ₂₀	54	156	3
C ₄₈ H ₅₀	98	242	9

EXAMPLE INPUT

The following input deck serves to illustrate the format required. The ground state geometry of formaldehyde (CH₂O) is optimised, the eigenvectors printed and the dipole matrix elements $\langle i|y|f \rangle$ are calculated for all occupied initial and unoccupied final states (but for spin up only, since the spin down elements will be identical in a singlet state). No external forces or fields are applied; the default method (CNDO) and length scale (Angstroms) are used.

TITLE

Ground state geometry of formaldehyde - also matrix elements

NUMBERS

4 0 1

GEOMETRY

6 0.0 0.0 0.0

8 1.2 0.0 0.0

1 -0.55 0.953 0.0

1 -0.55 -0.953 0.0

DAMPING

0.6 1.2

LIMITS

1.0E-4 1.0E-4 5.0 3 25

DIPOLE

PRINT

0 0 0 0 0 1

END

6

1 0 2

2 0 2

3 0 2

4 0 2

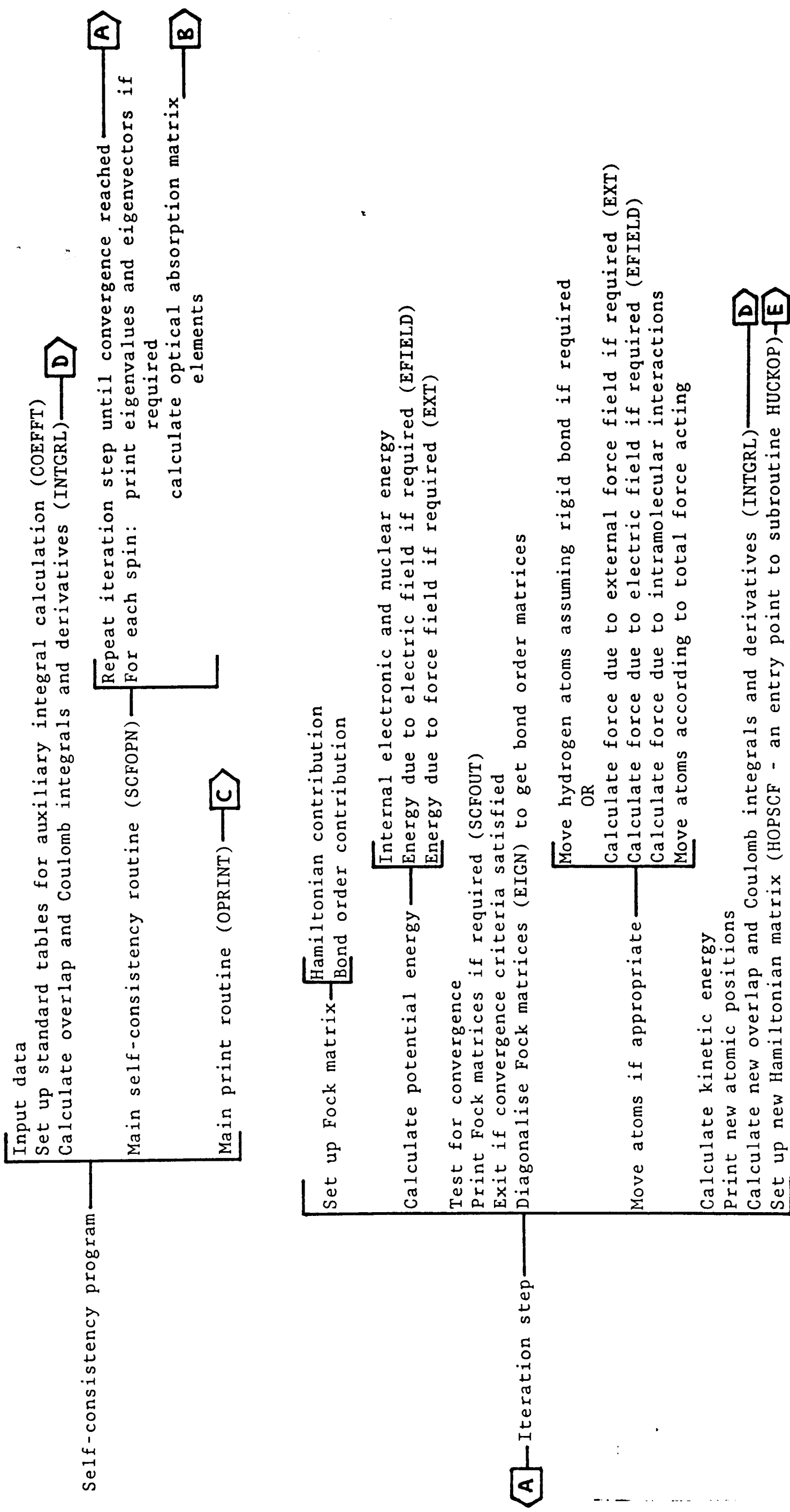
5 0 2

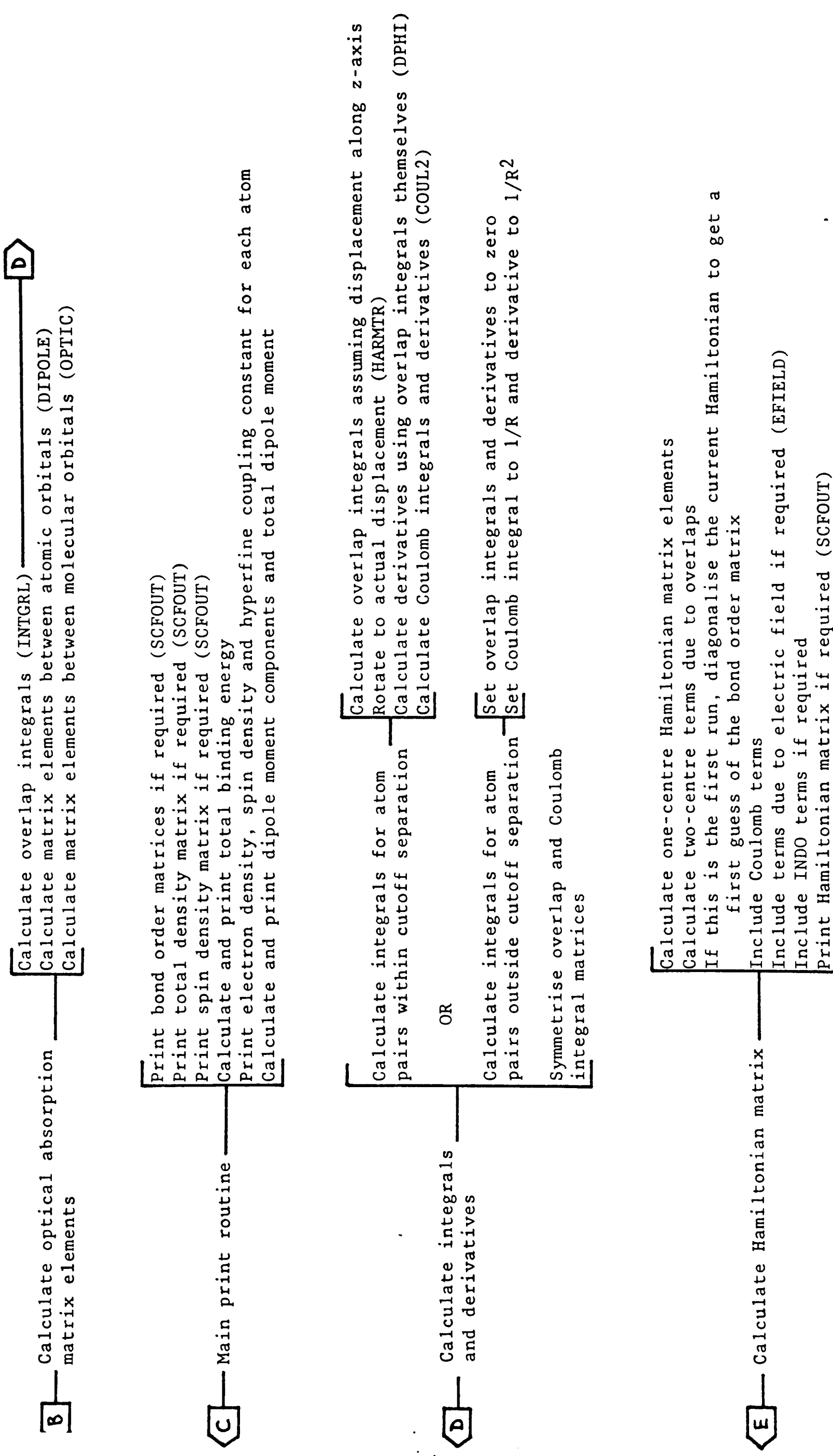
6 0 2

0

STRUCTURE CHART

A fairly high-level structure chart of the program is included on the next two pages; where a subroutine is called, its name is included in parentheses.





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