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An *ab initio* approach to determining the parameters of the model Hamiltonian $\hat{H}$

Rouli Fu†‡, M H Lee† and M C Payne†

† Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK
‡ National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 200083, People's Republic of China

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Abstract. By means of *ab initio* total-energy pseudopotential calculations, the parameters of the model Hamiltonian for *trans*-$(CH)_x$ are determined. The structural parameters of the ground state are obtained by relaxing the positions of the atoms and determining the lowest energy states for different lattice constants. The results are in agreement with experiments. Then, applying constraints to the system, we calculate the cohesive energies of dimerization for various dimerized displacements. Comparing these cohesive energies with those given by the model Hamiltonian, we determine the effective interaction strengths of the model Hamiltonian. With the above-mentioned parameters, the localized states of solitons are calculated. We find six localized soliton modes, three with odd parity and three with even parity. The former and the latter are, respectively, qualitatively consistent with the Raman and infrared spectra of the material.

1. Introduction

Conducting and semiconducting polymers are promising candidates as regards use in future optoelectronic devices and molecular devices. They display unusual magnetic and optical properties, most of which can be understood in terms of a simple effective model Hamiltonian [1–3]. Today, model Hamiltonians are widely used for describing the excited states of conducting polymers and fullerenes, since *ab initio* calculations are mainly suitable for ground states. Conventionally, the parameters in the model Hamiltonian are deduced via fittings to experimental data. However, experimental results for new materials are generally scarce and diverse, i.e. the experimental results tend to vary according to the experimental conditions. In contrast, *ab initio* calculations can be used to compute the total energy and other characteristic data of the ground state for any materials without experimental input. As computers become more powerful, determining the parameters of model Hamiltonians from *ab initio* calculations will eventually be more convenient and practicable than getting them from experiments.

Stollhoff [4], in his work on *ab initio* ground-state calculations with the local *ansatz*, used *ab initio* quantum chemistry calculations to obtain the parameters of the Su–Schrieffer–Heeger (SSH) [1] Hamiltonian.

The SSH model Hamiltonian is a tight-binding model with electron–phonon interactions:

$$H_{SSH} = H_e + \frac{1}{2}K\sum_n (u_{n+1} - u_n)^2$$

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$$= -\sum_{n,s}[t_0 - \alpha(u_{n+1} - u_n)](a^+_{n+1,s}a_{n,s} + \mathrm{HC}) + \frac{1}{2}K\sum_{n=1}^{N}(u_{n+1} - u_n)^2 \qquad (1)$$

where H_e is the electronic Hamiltonian; $a^+_{n,s}$ and $a_{n,s}$ are the creation and annihilation operators of an electron on site n with spin s; t_0 is the electron hopping constant; α is the electron–phonon coupling constant; u_n is the configuration coordinate for displacement of the nth (CH) unit from the position it is in when all the (CH) units are equally spaced; K is the elastic constant; and N is the number of (CH) units.

Specifically, Stollhoff [4] fitted the self-consistent-field (SCF) approximation ground-state energy of the model Hamiltonian to the SCF *ab initio* calculations. However, he used the empirical tight-binding result for the hopping constant $t_0 = 2.5$ eV as input, and consequently the bond alternation he obtained deviated from experimental results.

Springborg [5], applying the first-principles linear-muffin-tin-orbital (LMTO) method to the study of the electronic structure of polyacetylene, estimated t_0 and α of the SSH Hamiltonian by calculating the hopping integrals as functions of the interatomic distance and comparing them with the hopping integrals of the SSH model. However, the SSH Hamiltonian is a 1D model which takes only nearest-neighbour interactions into account and assumes that the hopping integrals are linearized around the value of the undimerization, whereas the LMTO Hamiltonian is an approximation to the density functional scheme. Since the Hamiltonian of the SSH model is different from that of the first-principles LMTO method, it is not appropriate to compare with them term by term. So, it is not surprising that the parameters t_0 and α which Springborg [5] obtained are somewhat different from those estimated from the experimental results. The effective interaction strengths in the model Hamiltonian should be deduced by fitting the data for the ground state obtained from the model Hamiltonian to the ground-state results for the material obtained from experiments or *ab initio* calculations.

Today, *ab initio* total-energy pseudopotential calculations, performed in the framework of density functional theory (DFT) and integrated by the pseudopotential approach, allow us to study systems at the atomic level. These calculations provide an effective and practical methodology for calculating the total energy of the ground state for any material. Hence, it is possible to get the parameters of the model Hamiltonian by fitting the ground-state results of the model Hamiltonian to *ab initio* total-energy pseudopotential calculations, instead of fitting them to data from experiments, which are, in some cases, becoming more expensive to obtain than calculated data. In this work, we use *ab initio* total-energy pseudopotential calculations to obtain the effective interaction strengths of the SSH model Hamiltonian and the structural parameters of the ground state for *trans*-$(\mathrm{CH})_x$. Also the calculated results are compared with the available experimental data.

2. Computations

The computations were carried out using the *ab initio* pseudopotential approach within the local density approximation (LDA) [6, 7] of the DFT. The Kohn–Sham equations were solved by expanding the wavefunctions in terms of a plane-wave basis and directly minimizing the total energy by using the conjugate-gradient technique [8]. We adopted a non-local norm-conserving *ab initio* pseudopotential [9] for carbon, particularly constructed to optimize the softness of the pseudopotential, so the size of the basis set needed to represent it was minimized. For hydrogen, the Coulomb potential was used. The calculations were performed on a single $(\mathrm{CH})_x$ chain in a supercell since the SSH Hamiltonian is a 1D model. The distance between chains in neighbouring supercells is larger than 7 Å, so the interaction of two chains can be neglected. The method of special $\boldsymbol{k}$-points [10] was used to perform the integrations in k-space over the first Brillouin zone. The plane-wave cut-off energy adopted in our calculations was 700 eV, which gave very good convergence for the total energy of the ground state, and thus we were able to determine the structural properties of the ground state correctly. When we performed *ab initio* calculations in this study, we focused on properties derived from total energies. All of the total-energy calculations were performed on $alpha$ workstations using the program CASTEP [11].

3. Fitting the parameters

3.1. Structural data for the ground state obtained from ab initio calculations

With the atomic numbers and atomic masses as input, we searched for the the equilibrium positions of the atoms and the lowest electronic energy states by relaxing the positions of atoms and changing the size of the unit cell (only the cell edge that is in the direction of the chain axis). The total energy $E(A)$ of the lowest energy state for any lattice constant A (in the direction of the chain axis) can be expressed as

$$E(A) = E_{ground} + \frac{1}{2}K(A - A_{ground})^2 \qquad (2)$$

where E_{ground} and A_{ground} are, respectively, the total energy and lattice constant of the ground state, and K is the elastic constant.

With the least-squares fit, we got E_{ground}, K and A_{ground} simultaneously. In the ground state, the calculated lattice constant in the direction of the chain axis is $A_{ground} = 2.443$ Å, while x-ray results give $A = 2.455$ Å [12] and 2.46 Å [13]. The calculated elastic constant $K = 21.540$ eV Å^{-2}, and the experimental value for K quoted in [5] is 21 eV Å^{-2}.

We obtained the ground state by relaxing the positions of atoms and changing the lattice constant, and with the method mentioned above. From the calculated ground state, we obtained the *trans*-$(\mathrm{CH})_x$ structure as shown in figure 1, on which the angles and unit cell are marked. The double-bond length is 1.35 Å, the single-bond length is 1.42 Å, and the C–H bond length is 1.10 Å. The corresponding x-ray results [12] are 1.36 Å, 1.45 Å, and 1.09 Å, respectively.

In the ground state, the dimerization displacement μ_0 is the displacement of a C atom projected onto the chain axis. From the position of the atoms in the ground state, the calculated displacement of the dimerization μ_0 is 0.0396 Å, whereas an NMR experiment yields $\mu_0 \simeq 0.035$ Å [14], and the x-ray results give $\mu_0 \simeq 0.052$ Å [12] and 0.03 Å [13]. The calculated dimerization stabilization energy E_{dim}, which is defined as the total energy per CH unit of the undimerized structure minus that of the optimized dimerized structure, is 0.0192 eV.

The experimental results cited here were measured on crystals, while our computations were performed for an isolated chain. There exist numerous theoretical estimates for the structural parameters of this material (see [15–21] and references therein). The available self-consistent LDA calculations also give different calculated values of μ_0 and E_{dim}: Springborg *et al* [16, 17] found $\mu_0 = 0.028$ Å, $E_{dim} = 0.056$ eV with 11 k-points; Mintmire and White [18] gave $\mu_0 = 0.016$ Å, $E_{dim} = 0.042$ eV with 11 k-points and $\mu_0 = 0.009$ Å, $E_{dim} = 0.006$ eV with 41 k-points; Ashkenazi *et al* [19] reported $\mu_0 = 0$, $E_{dim} = 0$ with 36 k-points; Vogl and Campbell [20] obtained $\mu_0 = 0.005$ Å with 15 k-points; Paloheimo and von Boehm [21] predicted $\mu_0 = 0.01$ Å, $E_{dim} = 0.007$ eV with 20 k-points and $\mu_0 = 0.015$ Å, $E_{dim} = 0.03$–0.04 eV with 11 k-points. Our result is $\mu_0 = 0.0396$ Å, $E_{dim} = 0.0192$ eV with 5 k-points, which are (0, 0, 0), (0.125, 0, 0), (0.25, 0, 0), (0.325,

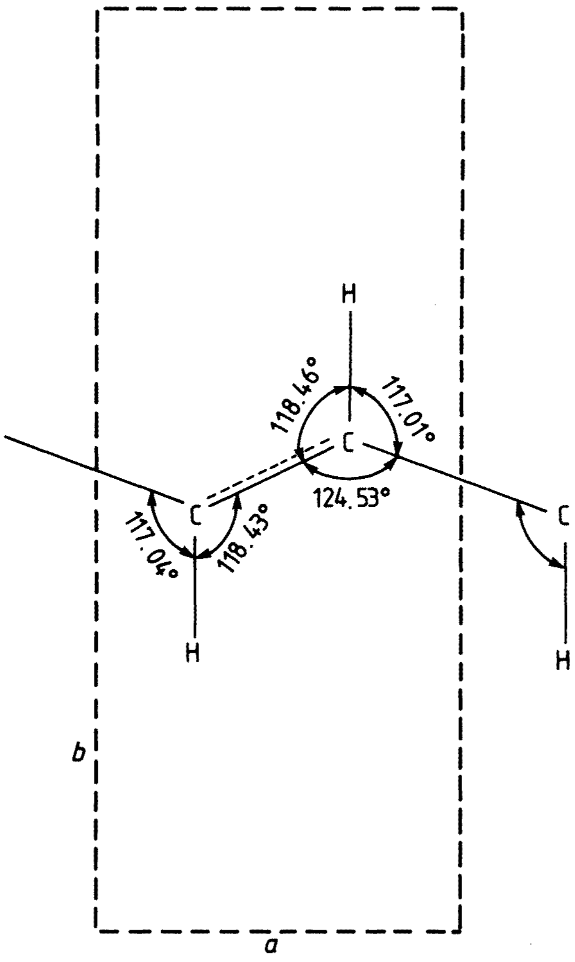

Figure 1. The structure of *trans*-$(CH)_x$ with optimized equilibrium positions of atoms. All the angles are given since the two C–H bonds are not perfectly parallel. The blocks surrounded by the broken lines are the unit cells in the calculations ($a = 2.443$ Å, which is optimized; b and c are fixed at $b = 10.0$ Å, $c = 7.0$Å).

0, 0) and (0.5, 0, 0) and whose weights are 0.125, 0.25, 0.25, 0.25 and 0.125, respectively. Among the above values, our μ_0 is the largest one, while our E_{dim} is just a medium value. Two of the features in the calculations are that the space group symmetry is not conserved during relaxation of the atoms in the unit cell and that the supercell is larger than others'. So this result implies that removing the constraint of space group symmetry conservation and isolating the interchain interaction will affect the values of μ_0 and E_{dim}.

3.2. Effective interaction strengths obtained from ab initio calculations

Since the energy zero for the model Hamiltonian is different from that for the first-principles calculations, we have to compare the dimerization-cohesive energies obtained from the model Hamiltonian with those obtained from the *ab initio* total-energy pseudopotential calculations, in order to determine the effective interaction strengths in the model

Hamiltonian.

In the dimerized state, $u_{n+1} = -u_n = \mu$ and equation (1) can be simplified as follows:

$$H_{SSH} = -\sum_{n,s} [t_0 + (-1)^n 2\alpha\mu](a^{+}_{n+1,s} a_{n,s} + \mathrm{HC}) + \frac{1}{2} NK(2\mu)^2 \tag{3}$$

where μ is the displacement of the dimerization.

After dimerization, the reduced Brillouin zone will cover the range of k-values $|k| \leqslant \pi/4a$. Taking the Fourier transform of the operators a_{odd} and a_{even} at odd and even sites, we diagonalize the first term of equation (4). Then transforming the second term of equation (4) again, we get new diagonal and non-diagonal elements. Upon setting the coefficient of the non-diagonal elements to zero, the analytical solution for the electronic spectra is

$$E(k) = \pm\sqrt{(2t_0 \cos(2ka))^2 + (4\alpha\mu \sin(2ka))^2} \tag{4}$$

where + (−) refers to the valence (conduction) band.

The total energy of the model Hamiltonian is a function of dimerization displacement and equals the electronic energy plus the lattice energy:

$$\begin{aligned} E(\mu) &= 2 \sum_{|k| \leqslant 1/4a} E_v(k) + \frac{1}{2} NK(2\mu)^2 \\ &= -4Na \int_0^{1/4a} \mathrm{d}k \sqrt{(2t_0 \cos(2ka))^2 + (4\alpha\mu \sin(2ka))^2} + \frac{1}{2} NK(2\mu)^2. \end{aligned} \tag{5}$$

The dimerization-cohesive energy, i.e. the variation of the total energy induced by the dimerization, equals

$$\Delta E(\mu) = E(\mu) - E(0). \tag{6}$$

When μ is quite small, equation (7) can be simplified to give

$$\Delta E(\mu) \simeq -\frac{8N}{\pi} \left(\ln\left(\frac{2t_0}{\alpha\mu} \right) - \frac{1}{2} \right) \frac{\alpha^2 \mu^2}{t_0} + 2NK\mu^2. \tag{7}$$

We also calculated the dimerization-cohesive energies $\Delta E(\mu)$ for various atomic displacements with *ab initio* total-energy pseudopotential calculations. For this purpose, we constrained the system in order to define different dimerized displacements. The constraints were applied in such a way that the hydrogen atoms can relax in all directions, and carbon atoms might relax only in the plane perpendicular to the constrained direction. Then we searched for the lowest energy state by relaxing the positions of atoms. The total-energy differences between the lowest energy state of the constrained system and the ground state are the dimerization-cohesive energies $\Delta E(\mu)$. In this way, a series of values of $\Delta E(\mu)$ were found for various dimerized displacements by using *ab initio* total-energy pseudopotential calculations. With the least-squares fit, we obtained an electron hopping constant $t_0 = 2.1995$ eV and an electron–phonon coupling constant $\alpha = 4.1552$ eV Å^{-1}.

4. Applying the above-mentioned parameters in the calculation of localized states of solitons

With the calculated parameters in hand, we took a ring of N (CH) units and the configuration

$$u_n = (-1)^n \mu_0 \tanh\left[\left(n - \frac{N+1}{2} \right) \Big/ \xi \right]$$

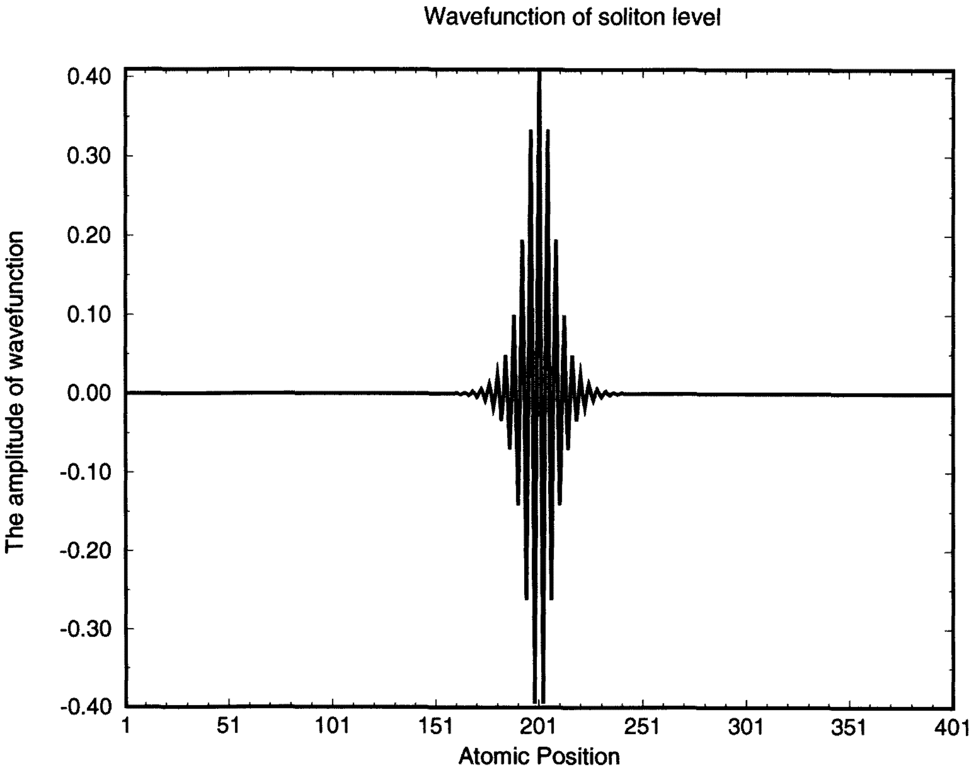

Figure 2. The electronic wavefunction of the soliton level.

as the initial trial soliton configuration, where ξA_{ground} is the soliton width. From the model Hamiltonian, equation (1), the eigenvalue ε_μ and the wavefunction $Z_{n,\mu}$ are obtained from the eigenequation

$$H_e Z_{n,\mu} = \varepsilon_\mu Z_{n,\mu}. \tag{8}$$

The static energy of the system is the electronic energy plus the elastic energy:

$$E(\{u_n\}) = \sum_{\mu}^{occ} \varepsilon_\mu(\{u_n\}) + \frac{1}{2} K \sum_{n=1}^{N} (u_{n+1} - u_n)^2. \tag{9}$$

Using the variational theorem,

$$\frac{\delta E(\{u_n\})}{\delta u_n} = 0 \tag{10}$$

we obtained the ground state. By using the initial trial soliton configuration

$$u_n = (-1)^n \mu_0 \tanh\left[\left(n - \frac{N+1}{2}\right)\Big/7\right]$$

and solving the simultaneous equations (8)–(10) by numerical iteration, we self-consistently found the real equilibrium positions $\{u_n^0\}$ of atoms, and the electronic eigenvalues and wavefunctions of a new ground state—the soliton. This soliton is a 1D domain wall that separates the two degenerate ground-state structures of the isomers for *trans*-polyacetylene [1].

A soliton will give rise the localized states in both the electron and phonon level spectra, since the soliton is a kind of self-localized carrier.

According to the calculated electronic wavefunction of the charged soliton, we found a localized state in the gap, which is the soliton level located near the midgap. Figure 2 shows the wavefunction of the soliton level. If the zero of energy is at the top of the valence band, the calculated soliton level is at 0.78 eV. Optical absorption spectra [22] showed that the soliton level occurs at about 0.7 eV.

To determine the vibrational modes of the soliton, we introduced small deviations δu_n from the equilibrium positions, since the calculated equilibrium positions $\{u_n^0\}$ are the static configurations of the soliton. In the small-deviation limit, we constructed the vibration matrix

$$V_{mn} = \frac{\delta^2 E(\{u_n\})}{\delta u_m \ \delta u_n}. \tag{11}$$

Let the eigenvalues and eigenvectors of matrix $\mathbf{V}$ be Λ_ν and $A_{n,\nu}$:

$$\sum_m V_{mn} A_{m,\nu} = \Lambda_\nu A_{n,\nu} \tag{12}$$

where the eigenvector $A_{n,\nu}$ represents the amplitude of the nth atom induced by the νth vibrational mode. The frequency of the νth vibrational mode is

$$\omega_\nu = \sqrt{\Lambda_\nu / M} \tag{13}$$

where M is the mass of a (CH) unit. By diagonalizing $\mathbf{V}$, we obtained all the vibrational modes of the soliton. Among these, we found six localized modes (instead of five found in [23]), whose eigenvectors and frequency values are shown in figures 3 and 4. Figure 4 shows that (a), (c) and (e) modes are of even parity; figure 3 shows that (b), (d) and (f) modes are of odd parity. The localized mode (f) is the new mode that has not previously been reported.

For the modes with odd parity, the atom at the centre of the soliton is fixed and the vibration of the other atoms has inversion symmetry about this centre. Therefore, the electric dipole moment is zero for the localized modes with odd parity. Hence, the localized modes (b), (d) and (f) are infrared inactive. Since infrared spectra and Raman spectra tend to be complementary, the localized modes (b), (d) and (f) are expected to be Raman active. These three localized modes are qualitatively consistent with the three lines observed in Raman spectra [2, 24].

The electric dipole moment is non-zero for the localized modes with even parity. So the localized modes (a), (c) and (e) are infrared active. These three localized modes are qualitatively consistent with the infrared experiment [25]. However, our calculated frequencies for the (a), (c) and (e) modes are at 0, 848 cm^{-1}, 898 cm^{-1}; while the experimental data [25] are 500 cm^{-1}, 1250 cm^{-1}, 1370 cm^{-1}. If we use the parameters of [1] or [2], the calculated frequencies for infrared-active localized modes are at 0, 798 cm^{-1}, 887 cm^{-1}, or 0, 1092 cm^{-1}, 1225 cm^{-1}. In previous work [23] calculating the infrared modes using the SSH Hamiltonian, the calculated frequencies were 0,1341 cm^{-1}, 1392 cm^{-1} when using somewhat artificial parameters [23]. These data show that it is an intrinsic problem of SSH model Hamiltonian that the calculated frequencies of localized modes are quantitatively inconsistent with the experiment. It also implies that we should adopt more accurate methods, i.e. *ab initio* calculations, to achieve quantitative agreement with the experimental results.

From figures 3 and 4 we can see that, if one wishes to obtain localized soliton modes by *ab initio* calculation, one should choose a large enough cluster—at least large enough to

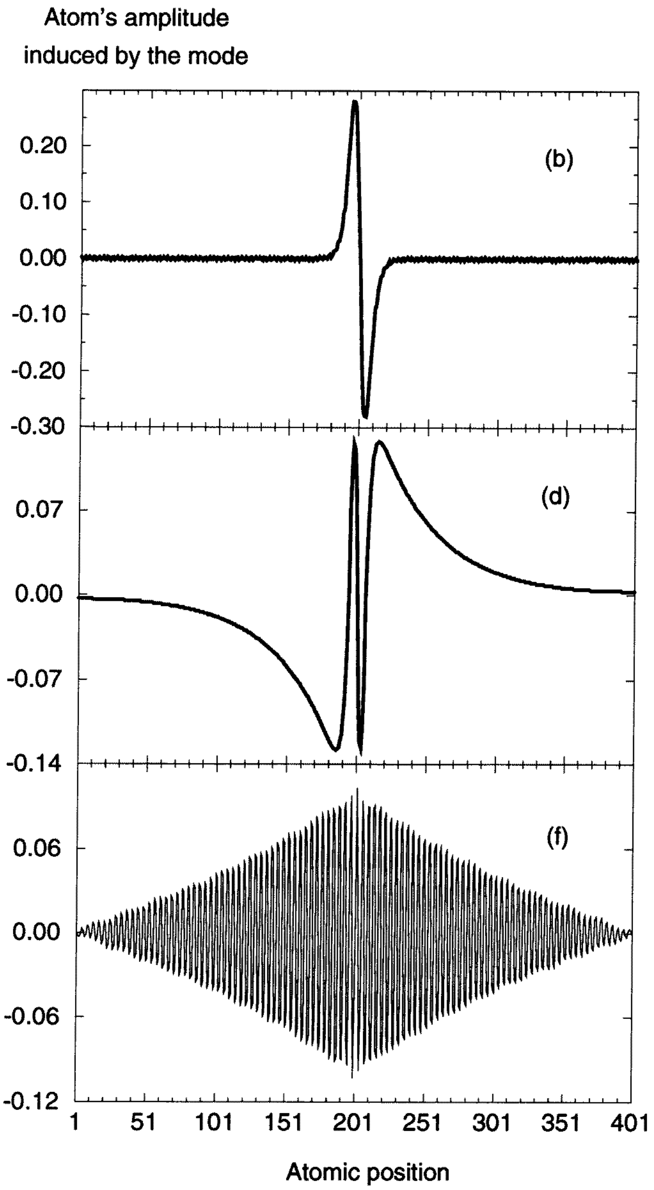

Figure 3. The localized modes (b), (d) and (f) with odd parity. The abscissa represents the atomic position and the ordinate represents the atom's displacement induced by the mode. The frequency values are 734 cm^{-1}, 880 cm^{-1}, 937 cm^{-1}.

include 101 (CH) units in the chain direction. On considering the increase of cpu time and memory with the increase of the number of atoms, it is clear that a powerful computer would be needed for such a calculation. Since this *ab initio* study only involves the dimerized state, there are only two (CH) units in a supercell. Thus, an average workstation is perfectly acceptable.

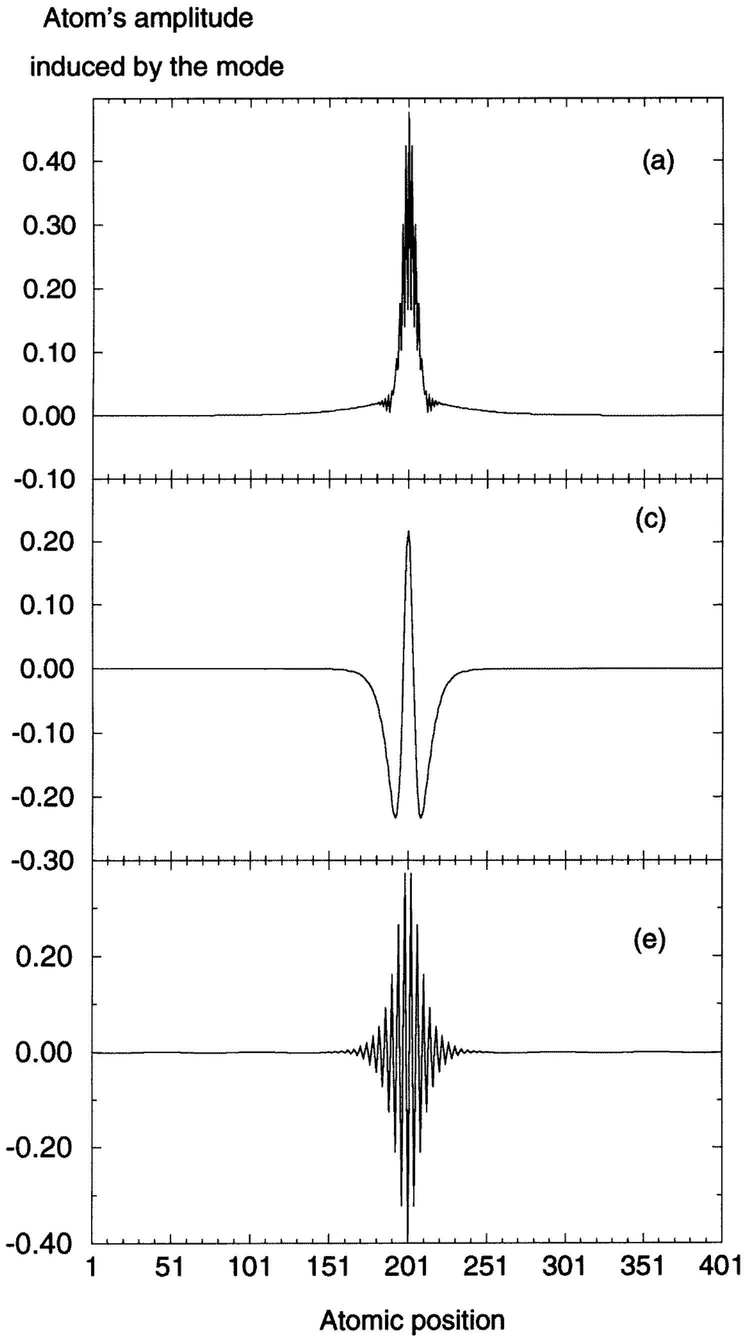

Figure 4. The localized modes (a), (c) and (e) with even parity. The abscissa represents the atomic position and the ordinate represents the atom's displacement induced by the mode. The frequency values are 0, 848 cm^{-1}, 898 cm^{-1}.

In summary, with no experimental input, we have obtained the structural parameters of the ground state and the effective interaction strengths of the model Hamiltonian. The structural parameters of the ground state are in agreement with relevant experiments. And with the above-mentioned parameters, the calculated localized states of the soliton are in qualitative agreement with the available experimental data.

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