TITLE: A THREE-DIMENSIONAL TIGHT-BINDING MODEL FOR TRANS-POLYACETYLENE

LA-UR--90-3329

AUTHOR(S): X. Wang
D. K. Campbell
H.-Q. Lin
P. Vogl

DE91 000182

SUBMITTED TO: Proceedings of the International Conference on Science and
Technology of Synthetic Metals ICSM'90, Tubigen (FRC),
September 2-7, 1990.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

A THREE-DIMENSIONAL TIGHT-BINDING MODEL FOR *trans*-POLYACETYLENE

X. WANG, D.K. CAMPBELL, and H.-Q. LIN

Center for Nonlinear Studies, Los Alamos National Laboratory, NM 87545

P. VOGL

Physik Dept., Technische Univ. München, 8046 Garching, W. Germany.

ABSTRACT

We develop a three-dimensional (3-D) generalization of the one-dimensional (1-D), tight-binding Su-Schrieffer-Heeger (SSH) model for *trans*-(CH)_x. Importantly, the model faithfully reflects the 3-D character of the band-edge states as found in *ab initio* Local-Density-Approximation (LDA) calculations but remains simple enough to be analytically solvable for the dimerized ground state. We examine the density of states and the optical absorption predicted within this model, paying special attention to the roles of the transverse coupling and the polarization of the probing field.

A THREE-DIMENSIONAL MODEL FOR POLYACETYLENE

Local-Density-Approximation (LDA) calculations [1,2] provide useful information about 3-D structure of polyacetylene. With this information, a simplified model can be constructed to study the effects of dimensionality on the optical absorption and dynamical properties, which are likely to remain inaccessible to first principles calculations. Fig. 1 shows the schematic structure of our model for a 3-D polyacetylene [1-3]. The corresponding tight-binding Hamiltonian can be written as

$$H = \sum_{\mathbf{r}} [t_l C^\dagger(\mathbf{r},1)C(\mathbf{r},4) + t_s C^\dagger(\mathbf{r}+\mathbf{e},1)C(\mathbf{r},4) + t_b C^\dagger(\mathbf{r},3)C(\mathbf{r},2) + t_{sl} C^\dagger(\mathbf{r}+\mathbf{e},3)C(\mathbf{r},2) + t_p [C^\dagger(\mathbf{r},2)C(\mathbf{r},4) + C^\dagger(\mathbf{r}-\mathbf{b},1)C(\mathbf{r},3) + C^\dagger(\mathbf{r}-\mathbf{a},4)C(\mathbf{r},2) + C^\dagger(\mathbf{r}-\mathbf{a}-\mathbf{b},1)C(\mathbf{r},3)]] + h.c. , \quad (1)$$

where $C^\dagger(\mathbf{r},i)$, $C(\mathbf{r},i)$ are the electron creation and annihilation operators of the i^{th} atom within the unit cell at position $\mathbf{r}$. t_l and t_s depend on the phonon coordinates of the lattice in the same way as in the SSH model of one-dimensional *trans*-(CH)_x model, i.e. $t_l = t_0 - \alpha u$ and $t_s = t_0 + \alpha u$. Here u is the displacement of the (CH) unit from its equilibrium position. Based on X-ray data (see [2] for complete references), two similar 3-D structures (both contained in Fig. 1) have been proposed for *trans*-(CH)_x: One is the $P2_1/a$ structure with $t_b \equiv t_l$ and $t_{sl} \equiv t_s$. The other one is the $P2_1/n$ structure with $t_b \equiv t_s$ and $t_{sl} \equiv t_l$; t_p is the transverse hopping integral between the chains. The numerical value of t_p is different in the two structures [1,2]. In the following, we focus only on the $P2_1/a$ structure, which is the predicted ground state within LDA [1-3].

where $|\phi(\mathbf{R}, i)\rangle$ is the i^{th} atomic wavefunction of the unit cell at location $\mathbf{R}$. Since the $\epsilon \cdot \nabla$ factor depends on the direction of the electromagnetic field polarization vector, we need to study optical absorption separately for the cases when ϵ is along different principal directions of our orthorhombic crystal model.

For the case when $\epsilon // c$, there are eight contributions to the transition matrix $T_{n,l}(\mathbf{k})$ from each unit cell. Because of the symmetry of the crystal structure, we can define $\langle \phi(\mathbf{r}, 3) | \nabla_c | \phi(\mathbf{r}, 2) \rangle = \langle \phi(\mathbf{r}, 2) | \nabla_c | \phi(\mathbf{r} + \mathbf{c}, 3) \rangle \equiv p_c$. By summing the eight terms, the transition matrix element becomes

$$T_{n,l}^c(\mathbf{k}) = p_c [(1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{1,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{4,n}^* U_{1,l} + (1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{3,n}^* U_{2,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{2,n}^* U_{3,l}]. \quad (4)$$

For the case when $\epsilon // a$, we assume the dipole moments which couple to the external field exist only where electron hopping exists, i.e. $\langle \phi(\mathbf{R}, i) | H_{\text{dipole}} | \phi(\mathbf{R}', j) \rangle$ is proportional to $\langle \phi(\mathbf{R}, i) | H | \phi(\mathbf{R}', j) \rangle$. With the definition $\langle \phi(\mathbf{r}, 2) | \nabla_a | \phi(\mathbf{r}, 4) \rangle = \langle \phi(\mathbf{r} - \mathbf{a}, 4) | \nabla_a | \phi(\mathbf{r}, 2) \rangle \equiv p_a$, we have

$$T_{n,l}^a(\mathbf{k}) = \sin(\theta) p_a [(1 - e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} + (e^{i\mathbf{k} \cdot \mathbf{b}} - e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} - (e^{-i\mathbf{k} \cdot \mathbf{b}} - e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}], \quad (5)$$

where θ is the angle indicated in Fig.1. Similarly, for the case when $\epsilon // b$, we obtain

$$T_{n,l}^b(\mathbf{k}) = \cos(\theta) p_b [(1 + e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 + e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} - (e^{i\mathbf{k} \cdot \mathbf{b}} + e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} + (e^{-i\mathbf{k} \cdot \mathbf{b}} + e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}]. \quad (6)$$

Up to a constant independent of the frequency, the optical absorption is the transition rate divided by the photon frequency,

$$\alpha(\omega) = \text{const.} \sum_{n=c,b,l} \sum_{v,b,k} \frac{1}{\omega} |T_{nl}(\mathbf{k})|^2 \delta(E_n(\mathbf{k}) - \omega - E_l(\mathbf{k})). \quad (7)$$

As for the density of states, we can find the optical absorption by using the histogram technique. The results of our calculations are plotted in Figs. 3-5.

SUMMARY

In summary, we have developed a 3-D generalization of the 1-D, tight-binding model for *trans*-(CH)_x. We have calculated the density of states and the optical absorption for different polarization of the probing fields. Further detailed studies are under way.

This work was supported by Los Alamos National Laboratory, the US DOE-OBES, and the Fond zur Erförderung Wissenschaftlichen Forschung of Austria.

REFERENCES

1. P. Vogl and D. Campbell, Phys. Rev. Lett. **62** 2012 (1989).
2. P. Vogl and D. Campbell, Phys. Rev. B **41** 12797 (1990).
3. P. Vogl and D. Campbell, p. 151-164, *Interacting Electrons in Reduced Dimensions*, ed. D. Baeriswyl and D. Campbell, Plenum (1990).
4. J. Callaway, chap. 6, *Quantum Theory of the Solid State*, Academic Press Inc. (1974).

ENERGY BAND STRUCTURE AND DENSITY OF STATES

Transforming the Hamiltonian into reciprocal space by forming Bloch states $C(\mathbf{k}, i)$ from the $C(\mathbf{r}, i)$, one finally obtains a 4 by 4 Hamiltonian matrix in $\mathbf{k}$ space [3]. The 4 eigenvalues of $H(\mathbf{k})$ are

Fig. 1. The schematic unit cell of the three-dimensional polyacetylene crystal. The four solid dots represent the four carbon atoms in the unit cell at position $\mathbf{r}$. The heavy solid lines represent the bonds in c direction. The heavy dotted lines represent the allowed transverse hoppings between the chains. 1, 2, 3 and 4 are labels for the carbon atoms in the unit cell. a, b and c are labels for the principal directions of the crystal, which following [3] we take for simplicity to be orthogonal. The angle θ occurs in the text.

$$E(\mathbf{k}) = \pm [T_1^2 + T_2^2 \pm 2T_1T_2 \cos(\pi k_b)]^{\frac{1}{2}}, \quad (2a)$$

where we have defined

$$T_1^2 \equiv t_s^2 + t_l^2 + 2t_s t_l \cos(2\pi k_c), \quad T_2^2 = 4t_p^2 \cos^2(\pi k_a). \quad (2b)$$

The density of states can be calculated by scanning the $\mathbf{k}$ variables within the Brillouin zone and plotting a histogram of the energy level distribution. In Fig. 2, we show the density of states as a function of t_p .

OPTICAL ABSORPTION

The optical absorption can be calculated from the transition rate between the valence and the conduction bands. The transition matrix element between the two bands is given by [4] $\langle \tilde{\Psi}_n(\mathbf{k}) | H_{dipole} | \tilde{\Psi}_l(\mathbf{k}) \rangle$, where H_{dipole} can be written as $-\frac{ie\hbar}{m} \mathbf{A} \cdot \nabla$. Here $\mathbf{e}$ is the electromagnetic field polarization vector, and $|\tilde{\Psi}_l(\mathbf{k})\rangle$ is the wavefunction of the l^{th} band after diagonalizing the Hamiltonian (1). Substituting the expression for $|\tilde{\Psi}_l(\mathbf{k})\rangle$ into the transition matrix element, we find,

$$T_{n,l} \equiv \langle \tilde{\Psi}_n | \mathbf{e} \cdot \nabla | \tilde{\Psi}_l \rangle = \sum_{i,j} U_{i,n}^* U_{j,l} \langle 0 | C(\mathbf{k}, i) (\mathbf{e} \cdot \nabla) C^\dagger(\mathbf{k}, j) | 0 \rangle, \quad (3a)$$

where $C^\dagger(\mathbf{k}, i)$ and $C(\mathbf{k}, i)$ are the creation and annihilation operators for i^{th} band, and the matrix U is the unitary matrix which diagonalizes the Hamiltonian (1). Transforming back to the atomic wavefunction representation, we find the above matrix element can be written as

$$T_{n,l}(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}', i, j} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} U_{i,n}^* U_{j,l} \langle \phi(\mathbf{R}, i) | \mathbf{e} \cdot \nabla | \phi(\mathbf{R}', j) \rangle, \quad (3b)$$

Fig. 2. The density of states as a function of energy. The dotted, solid and dashed lines are for $t_p = 0.0, 0.12$ and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 3. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the c direction. The dotted, solid and dashed lines are for $t_p = 0.0, 0.12$ and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 4. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the a direction. The dotted, solid and dashed lines are for $t_p = 0.0, 0.12$ and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 5. Optical absorption spectrum for the case when the vector ϵ (see text) of the probing field is polarized along b direction. The dotted, solid and dashed lines are for $t_p = 0.0, 0.12$ and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

A THREE-DIMENSIONAL TIGHT-BINDING MODEL FOR *trans*-POLYACETYLENE

X. WANG, D.K. CAMPBELL, and H.-Q. LIN

Center for Nonlinear Studies, Los Alamos National Laboratory, NM 87545

P. VOGL

Physik Dept., Technische Univ. München, 8046 Garching, W. Germany.

ABSTRACT

We develop a three-dimensional (3-D) generalization of the one-dimensional (1-D), tight-binding Su-Schrieffer-Heeger (SSH) model for *trans*-(CH)_x. Importantly, the model faithfully reflects the 3-D character of the band-edge states as found in *ab initio* Local-Density-Approximation (LDA) calculations but remains simple enough to be analytically solvable for the dimerized ground state. We examine the density of states and the optical absorption predicted within this model, paying special attention to the roles of the transverse coupling and the polarization of the probing field.

A THREE-DIMENSIONAL MODEL FOR POLYACETYLENE

Local-Density-Approximation (LDA) calculations [1,2] provide useful information about 3-D structure of polyacetylene. With this information, a simplified model can be constructed to study the effects of dimensionality on the optical absorption and dynamical properties, which are likely to remain inaccessible to first principles calculations. Fig. 1 shows the schematic structure of our model for a 3-D polyacetylene [1-3]. The corresponding tight-binding Hamiltonian can be written as

$$H = \sum_{\mathbf{r}} \{ t_l C^\dagger(\mathbf{r},1)C(\mathbf{r},4) + t_s C^\dagger(\mathbf{r}+\mathbf{c},1)C(\mathbf{r},4) + t_{ls} C^\dagger(\mathbf{r},3)C(\mathbf{r},2) + t_{sl} C^\dagger(\mathbf{r}+\mathbf{c},3)C(\mathbf{r},2) \\ + t_p [C^\dagger(\mathbf{r},2)C(\mathbf{r},4) + C^\dagger(\mathbf{r}-\mathbf{b},1)C(\mathbf{r},3) + C^\dagger(\mathbf{r}-\mathbf{a},4)C(\mathbf{r},2) + C^\dagger(\mathbf{r}-\mathbf{a}-\mathbf{b},1)C(\mathbf{r},3)] \} + h.c. , \quad (1)$$

where $C^\dagger(\mathbf{r},i)$, $C(\mathbf{r},i)$ are the electron creation and annihilation operators of the i^{th} atom within the unit cell at position $\mathbf{r}$. t_l and t_s depend on the phonon coordinates of the lattice in the same way as in the SSH model of one-dimensional *trans*-(CH)_x model, i.e. $t_l = t_0 - \alpha u$ and $t_s = t_0 + \alpha u$. Here u is the displacement of the (CH) unit from its equilibrium position. Based on X-ray data (see [2] for complete references), two similar 3-D structures (both contained in Fig. 1) have been proposed for *trans*-(CH)_x: One is the $P2_1/a$ structure with $t_{ls} \equiv t_l$ and $t_{sl} \equiv t_s$. The other one is the $P2_1/n$ structure with $t_{ls} = t_s$ and $t_{sl} = t_l$; t_p is the transverse hopping integral between the chains. The numerical value of t_p is different in the two structures [1,2]. In the following, we focus only on the $P2_1/a$ structure, which is the predicted ground state within LDA [1-3].

where $|\phi(\mathbf{R}, i)\rangle$ is the i^{th} atomic wavefunction of the unit cell at location $\mathbf{R}$. Since the $\epsilon \cdot \nabla$ factor depends on the direction of the electromagnetic field polarization vector, we need to study optical absorption separately for the cases when ϵ is along different principal directions of our orthorhombic crystal model.

For the case when $\epsilon // c$, there are eight contributions to the transition matrix $T_{n,l}(\mathbf{k})$ from each unit cell. Because of the symmetry of the crystal structure, we can define $\langle \phi(\mathbf{r}, 3) | \nabla_c | \phi(\mathbf{r}, 2) \rangle = \langle \phi(\mathbf{r}, 2) | \nabla_c | \phi(\mathbf{r} + \mathbf{c}, 3) \rangle \equiv p_c$. By summing the eight terms, the transition matrix element becomes

$$T_{n,l}^c(\mathbf{k}) = p_c [(1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{1,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{4,n}^* U_{1,l} + (1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{3,n}^* U_{2,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{2,n}^* U_{3,l}]. \quad (4)$$

For the case when $\epsilon // a$, we assume the dipole moments which couple to the external field exist only where electron hopping exists, i.e. $\langle \phi(\mathbf{R}, i) | H_{\text{dipole}} | \phi(\mathbf{R}', j) \rangle$ is proportional to $\langle \phi(\mathbf{R}, i) | H | \phi(\mathbf{R}', j) \rangle$. With the definition $\langle \phi(\mathbf{r}, 2) | \nabla_a | \phi(\mathbf{r}, 4) \rangle = \langle \phi(\mathbf{r} - \mathbf{a}, 4) | \nabla_a | \phi(\mathbf{r}, 2) \rangle \equiv p_a$, we have

$$T_{n,l}^a(\mathbf{k}) = \sin(\theta) p_a [(1 - e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} + (e^{i\mathbf{k} \cdot \mathbf{b}} - e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} - (e^{-i\mathbf{k} \cdot \mathbf{b}} - e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}], \quad (5)$$

where θ is the angle indicated in Fig.1. Similarly, for the case when $\epsilon // b$, we obtain

$$T_{n,l}^b(\mathbf{k}) = \cos(\theta) p_a [(1 + e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 + e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} - (e^{i\mathbf{k} \cdot \mathbf{b}} + e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} + (e^{-i\mathbf{k} \cdot \mathbf{b}} + e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}]. \quad (6)$$

Up to a constant independent of the frequency, the optical absorption is the transition rate divided by the photon frequency,

$$\alpha(\omega) = \text{const.} \sum_{n=c,b, l=v,b, \mathbf{k}} \frac{1}{\omega} |T_{n,l}(\mathbf{k})|^2 \delta(E_n(\mathbf{k}) - \omega - E_l(\mathbf{k})). \quad (7)$$

As for the density of states, we can find the optical absorption by using the histogram technique. The results of our calculations are plotted in Figs. 3-5.

SUMMARY

In summary, we have developed a 3-D generalization of the 1-D, tight-binding model for *trans*-(CH)_x. We have calculated the density of states and the optical absorption for different polarization of the probing fields. Further detailed studies are under way.

This work was supported by Los Alamos National Laboratory, the US DOE-OBES, and the Fond zur Erförderung Wissenschaftlichen Forschung of Austria.

REFERENCES

1. P. Vogl and D. Campbell, Phys. Rev. Lett. **62** 2012 (1989).
2. P. Vogl and D. Campbell, Phys. Rev. B **41** 12797 (1990).
3. P. Vogl and D. Campbell, p. 151-164, *Interacting Electrons in Reduced Dimensions*, ed. D. Baeriswyl and D. Campbell, Plenum (1990).
4. J. Callaway, chap. 6, *Quantum Theory of the Solid State*, Academic Press Inc. (1974).

ENERGY BAND STRUCTURE AND DENSITY OF STATES

Transforming the Hamiltonian into reciprocal space by forming Bloch states $C(\mathbf{k}, i)$ from the $C(\mathbf{r}, i)$, one finally obtains a 4 by 4 Hamiltonian matrix in $\mathbf{k}$ space [3]. The 4 eigenvalues of $H(\mathbf{k})$ are

Fig. 1. The schematic unit cell of the three-dimensional polyacetylene crystal. The four solid dots represent the four carbon atoms in the unit cell at position $\mathbf{r}$. The heavy solid lines represent the bonds in c direction. The heavy dotted lines represent the allowed transverse hoppings between the chains. 1, 2, 3 and 4 are labels for the carbon atoms in the unit cell. a, b and c are labels for the principal directions of the crystal, which following [3] we take for simplicity to be orthogonal. The angle θ occurs in the text.

$$E(\mathbf{k}) = \pm [T_1^2 + T_2^2 \pm 2T_1T_2 \cos(\pi k_b)]^{\frac{1}{2}}, \quad (2a)$$

where we have defined

$$T_1^2 \equiv t_s^2 + t_l^2 + 2t_s t_l \cos(2\pi k_c), \quad T_2^2 = 4t_p^2 \cos^2(\pi k_a). \quad (2b)$$

The density of states can be calculated by scanning the $\mathbf{k}$ variables within the Brillouin zone and plotting a histogram of the energy level distribution. In Fig. 2, we show the density of states as a function of t_p .

OPTICAL ABSORPTION

The optical absorption can be calculated from the transition rate between the valence and the conduction bands. The transition matrix element between the two bands is given by [4] $\langle \tilde{\Psi}_n(\mathbf{k}) | H_{dipole} | \tilde{\Psi}_l(\mathbf{k}) \rangle$, where H_{dipole} can be written as $-\frac{ie\hbar}{m} \mathbf{A} \cdot \nabla$. Here $\mathbf{e}$ is the electromagnetic field polarization vector, and $|\tilde{\Psi}_l(\mathbf{k})\rangle$ is the wavefunction of the l^{th} band after diagonalizing the Hamiltonian (1). Substituting the expression for $|\tilde{\Psi}_l(\mathbf{k})\rangle$ into the transition matrix element, we find,

$$T_{n,l} \equiv \langle \tilde{\Psi}_n | \mathbf{e} \cdot \nabla | \tilde{\Psi}_l \rangle = \sum_{i,j} U_{i,n}^* U_{j,l} \langle 0 | C(\mathbf{k}, i) (\mathbf{e} \cdot \nabla) C^\dagger(\mathbf{k}, j) | 0 \rangle, \quad (3a)$$

where $C^\dagger(\mathbf{k}, i)$ and $C(\mathbf{k}, i)$ are the creation and annihilation operators for i^{th} band, and the matrix U is the unitary matrix which diagonalizes the Hamiltonian (1). Transforming back to the atomic wavefunction representation, we find the above matrix element can be written as

$$T_{n,l}(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}', i, j} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} U_{i,n}^* U_{j,l} \langle \phi(\mathbf{R}, i) | \mathbf{e} \cdot \nabla | \phi(\mathbf{R}', j) \rangle, \quad (3b)$$

Fig. 2. The density of states as a function of energy. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 3. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the c direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 4. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the a direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 5. Optical absorption spectrum for the case when the vector ϵ (see text) of the probing field is polarized along b direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

A THREE-DIMENSIONAL TIGHT-BINDING MODEL FOR *trans*-POLYACETYLENE

X. WANG, D.K. CAMPBELL, and H.-Q. LIN

Center for Nonlinear Studies, Los Alamos National Laboratory, NM 87545

P. VOGL

Physik Dept., Technische Univ. München, 8046 Garching, W. Germany.

ABSTRACT

We develop a three-dimensional (3-D) generalization of the one-dimensional (1-D), tight-binding Su-Schrieffer-Heeger (SSH) model for *trans*-(CH)_x. Importantly, the model faithfully reflects the 3-D character of the band-edge states as found in *ab initio* Local-Density-Approximation (LDA) calculations but remains simple enough to be analytically solvable for the dimerized ground state. We examine the density of states and the optical absorption predicted within this model, paying special attention to the roles of the transverse coupling and the polarization of the probing field.

A THREE-DIMENSIONAL MODEL FOR POLYACETYLENE

Local-Density-Approximation (LDA) calculations [1,2] provide useful information about 3-D structure of polyacetylene. With this information, a simplified model can be constructed to study the effects of dimensionality on the optical absorption and dynamical properties, which are likely to remain inaccessible to first principles calculations. Fig. 1 shows the schematic structure of our model for a 3-D polyacetylene [1-3]. The corresponding tight-binding Hamiltonian can be written as

$$H = \sum_{\mathbf{r}} [t_l C^\dagger(\mathbf{r},1)C(\mathbf{r},4) + t_s C^\dagger(\mathbf{r}+\mathbf{e},1)C(\mathbf{r},4) + t_b C^\dagger(\mathbf{r},3)C(\mathbf{r},2) + t_{sl} C^\dagger(\mathbf{r}+\mathbf{e},3)C(\mathbf{r},2) + t_p [C^\dagger(\mathbf{r},2)C(\mathbf{r},4) + C^\dagger(\mathbf{r}-\mathbf{b},1)C(\mathbf{r},3) + C^\dagger(\mathbf{r}-\mathbf{a},4)C(\mathbf{r},2) + C^\dagger(\mathbf{r}-\mathbf{a}-\mathbf{b},1)C(\mathbf{r},3)]] + h.c. , \quad (1)$$

where $C^\dagger(\mathbf{r},i)$, $C(\mathbf{r},i)$ are the electron creation and annihilation operators of the i^{th} atom within the unit cell at position $\mathbf{r}$. t_l and t_s depend on the phonon coordinates of the lattice in the same way as in the SSH model of one-dimensional *trans*-(CH)_x model, i.e. $t_l = t_0 - \alpha u$ and $t_s = t_0 + \alpha u$. Here u is the displacement of the (CH) unit from its equilibrium position. Based on X-ray data (see [2] for complete references), two similar 3-D structures (both contained in Fig. 1) have been proposed for *trans*-(CH)_x: One is the $P2_1/a$ structure with $t_b \equiv t_l$ and $t_{sl} \equiv t_s$. The other one is the $P2_1/n$ structure with $t_b \equiv t_s$ and $t_{sl} \equiv t_l$; t_p is the transverse hopping integral between the chains. The numerical value of t_p is different in the two structures [1,2]. In the following, we focus only on the $P2_1/a$ structure, which is the predicted ground state within LDA [1-3].

where $|\phi(\mathbf{R}, i)\rangle$ is the i^{th} atomic wavefunction of the unit cell at location $\mathbf{R}$. Since the $\epsilon \cdot \nabla$ factor depends on the direction of the electromagnetic field polarization vector, we need to study optical absorption separately for the cases when ϵ is along different principal directions of our orthorhombic crystal model.

For the case when $\epsilon // c$, there are eight contributions to the transition matrix $T_{n,l}(\mathbf{k})$ from each unit cell. Because of the symmetry of the crystal structure, we can define $\langle \phi(\mathbf{r}, 3) | \nabla_c | \phi(\mathbf{r}, 2) \rangle = \langle \phi(\mathbf{r}, 2) | \nabla_c | \phi(\mathbf{r} + \mathbf{c}, 3) \rangle \equiv p_c$. By summing the eight terms, the transition matrix element becomes

$$T_{n,l}^c(\mathbf{k}) = p_c [(1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{1,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{4,n}^* U_{1,l} + (1 - e^{i\mathbf{k} \cdot \mathbf{c}}) U_{3,n}^* U_{2,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{c}}) U_{2,n}^* U_{3,l}]. \quad (4)$$

For the case when $\epsilon // a$, we assume the dipole moments which couple to the external field exist only where electron hopping exists, i.e. $\langle \phi(\mathbf{R}, i) | H_{\text{dipole}} | \phi(\mathbf{R}', j) \rangle$ is proportional to $\langle \phi(\mathbf{R}, i) | H | \phi(\mathbf{R}', j) \rangle$. With the definition $\langle \phi(\mathbf{r}, 2) | \nabla_a | \phi(\mathbf{r}, 4) \rangle = \langle \phi(\mathbf{r} - \mathbf{a}, 4) | \nabla_a | \phi(\mathbf{r}, 2) \rangle \equiv p_a$, we have

$$T_{n,l}^a(\mathbf{k}) = \sin(\theta) p_a [(1 - e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 - e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} + (e^{i\mathbf{k} \cdot \mathbf{b}} - e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} - (e^{-i\mathbf{k} \cdot \mathbf{b}} - e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}], \quad (5)$$

where θ is the angle indicated in Fig.1. Similarly, for the case when $\epsilon // b$, we obtain

$$T_{n,l}^b(\mathbf{k}) = \cos(\theta) p_a [(1 + e^{i\mathbf{k} \cdot \mathbf{a}}) U_{2,n}^* U_{4,l} - (1 + e^{-i\mathbf{k} \cdot \mathbf{a}}) U_{4,n}^* U_{2,l} - (e^{i\mathbf{k} \cdot \mathbf{b}} + e^{i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{3,n}^* U_{1,l} + (e^{-i\mathbf{k} \cdot \mathbf{b}} + e^{-i\mathbf{k} \cdot (\mathbf{a} + \mathbf{b})}) U_{1,n}^* U_{3,l}]. \quad (6)$$

Up to a constant independent of the frequency, the optical absorption is the transition rate divided by the photon frequency,

$$\alpha(\omega) = \text{const.} \sum_{n=c,b,l} \sum_{m=v,b,l} \frac{1}{\omega} |T_{nl}(\mathbf{k})|^2 \delta(E_n(\mathbf{k}) - \omega - E_l(\mathbf{k})). \quad (7)$$

As for the density of states, we can find the optical absorption by using the histogram technique. The results of our calculations are plotted in Figs. 3-5.

SUMMARY

In summary, we have developed a 3-D generalization of the 1-D, tight-binding model for *trans*-(CH)_x. We have calculated the density of states and the optical absorption for different polarization of the probing fields. Further detailed studies are under way.

This work was supported by Los Alamos National Laboratory, the US DOE-OBES, and the Fond zur Erförderung Wissenschaftlichen Forschung of Austria.

REFERENCES

1. P. Vogl and D. Campbell, Phys. Rev. Lett. **62** 2012 (1989).
2. P. Vogl and D. Campbell, Phys. Rev. B **41** 12797 (1990).
3. P. Vogl and D. Campbell, p. 151-164, *Interacting Electrons in Reduced Dimensions*, ed. D. Baeriswyl and D. Campbell, Plenum (1990).
4. J. Callaway, chap. 6, *Quantum Theory of the Solid State*, Academic Press Inc. (1974).

ENERGY BAND STRUCTURE AND DENSITY OF STATES

Transforming the Hamiltonian into reciprocal space by forming Bloch states $C(\mathbf{k}, i)$ from the $C(\mathbf{r}, i)$, one finally obtains a 4 by 4 Hamiltonian matrix in $\mathbf{k}$ space [3]. The 4 eigenvalues of $H(\mathbf{k})$ are

Fig. 1. The schematic unit cell of the three-dimensional polyacetylene crystal. The four solid dots represent the four carbon atoms in the unit cell at position $\mathbf{r}$. The heavy solid lines represent the bonds in c direction. The heavy dotted lines represent the allowed transverse hoppings between the chains. 1, 2, 3 and 4 are labels for the carbon atoms in the unit cell. a, b and c are labels for the principal directions of the crystal, which following [3] we take for simplicity to be orthogonal. The angle θ occurs in the text.

$$E(\mathbf{k}) = \pm [T_1^2 + T_2^2 \pm 2T_1T_2 \cos(\pi k_b)]^{\frac{1}{2}}, \quad (2a)$$

where we have defined

$$T_1^2 \equiv t_s^2 + t_l^2 + 2t_s t_l \cos(2\pi k_c), \quad T_2^2 = 4t_p^2 \cos^2(\pi k_a). \quad (2b)$$

The density of states can be calculated by scanning the $\mathbf{k}$ variables within the Brillouin zone and plotting a histogram of the energy level distribution. In Fig. 2, we show the density of states as a function of t_p .

OPTICAL ABSORPTION

The optical absorption can be calculated from the transition rate between the valence and the conduction bands. The transition matrix element between the two bands is given by [4] $\langle \tilde{\Psi}_n(\mathbf{k}) | H_{dipole} | \tilde{\Psi}_l(\mathbf{k}) \rangle$, where H_{dipole} can be written as $-\frac{ie\hbar}{m} \mathbf{A} \cdot \nabla$. Here $\mathbf{e}$ is the electromagnetic field polarization vector, and $|\tilde{\Psi}_l(\mathbf{k})\rangle$ is the wavefunction of the l^{th} band after diagonalizing the Hamiltonian (1). Substituting the expression for $|\tilde{\Psi}_l(\mathbf{k})\rangle$ into the transition matrix element, we find,

$$T_{n,l} \equiv \langle \tilde{\Psi}_n | \mathbf{e} \cdot \nabla | \tilde{\Psi}_l \rangle = \sum_{i,j} U_{i,n}^* U_{j,l} \langle 0 | C(\mathbf{k}, i) (\mathbf{e} \cdot \nabla) C^\dagger(\mathbf{k}, j) | 0 \rangle, \quad (3a)$$

where $C^\dagger(\mathbf{k}, i)$ and $C(\mathbf{k}, i)$ are the creation and annihilation operators for i^{th} band, and the matrix U is the unitary matrix which diagonalizes the Hamiltonian (1). Transforming back to the atomic wavefunction representation, we find the above matrix element can be written as

$$T_{n,l}(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{R}, \mathbf{R}', i, j} e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')} U_{i,n}^* U_{j,l} \langle \phi(\mathbf{R}, i) | \mathbf{e} \cdot \nabla | \phi(\mathbf{R}', j) \rangle, \quad (3b)$$

Fig. 2. The density of states as a function of energy. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 3. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the c direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 4. Optical absorption spectrum for the case when the polarization vector ϵ (see text) of the probing field is polarized along the a direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

Fig. 5. Optical absorption spectrum for the case when the vector ϵ (see text) of the probing field is polarized along b direction. The dotted, solid and dashed lines are for $t_p = 0.0$, 0.12 and 0.36 respectively. The solid line is for the t_p deduced from fits to the LDA calculations [1,2].

END

DATE FILMED

10 / 26 / 90