

不同边界条件下导电高分子电子结构的研究*

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摘 要 用一维复式晶格作为反式聚乙炔的模型,在周期与非周期边界条件下,考虑链端效应并计及电子的非近邻跳跃,数值计算了格点数分别等于 $N = 10, 50, 100$ 和 200 时聚乙炔的能谱和态密度. 讨论了不同格点数和结构参数对态密度及带宽的影响,并对两种边界条件下的计算结果进行了比较. 计算结果表明,当格点数 $N < 50$ 时,两者相差较大,这表明系统的边界将起很大作用;当格点数 $N \geq 50$ 时,两者相差甚微,这时可利用周期性边界条件来研究有限系统问题.

关键词 复式晶格, 态密度, 表面态, 链端效应

导电高分子具有链状结构,是准一维体系. 反式聚乙炔 (*trans*-Polyacetylene) 的分子链是典型的准一维体系,主链由碳原子组成,每个碳原子有一个电子. 由于电子和晶格原子的相互作用,一维晶格具有 Peierls 不稳定性^[1],晶格要发生畸变. 畸变后每两个原子靠近一些,配成一对,即为二聚化 (Dimerization). 二聚化后,碳原子间的距离不再相等,距离远的两个碳原子之间形成长键,距离近的形成短键. 所以聚乙炔具有长、短键交替的结构,如图 1 所示. 在理论研究方面,随着 TLM^[2] 模型和 SSH^[3] 模型的问世,人们对导电高分子的研究有了突破性的进展,提出了在高聚物中建立孤子和极化子的概念,并成功地解释了聚合物的导电机理^[4,5]. 近年来,Subbaswamy 等^[6] 在 SSH 模型基础上引进了 Hubbard 模型^[7],计算电子间相互作用对单孤子能级的修正, Wu 等^[8] 研究电子相互作用对反式聚乙炔孤子定域态的影响,两者结果都说明引进电子相互作用对解释反式聚乙炔的性质是重要的. 这些工作几乎都是认为链是无限长的,即利用了周期性边界条件. 近年来的大量实验表明,实际聚乙炔材料中存在各种共轭缺陷,如 sp^3 键,使得分子链长度很短. Raman 散射实验表明分子链长度为 40 个 CH 基团甚至更短^[9],光致发光研究也得出平均长度可能少于 26 个 CH 基团的结论^[10]. 聚乙炔的链长是有限的,因此应该考虑链端效应,即边界条件是非周期性的. 基于这一情

况,孙国昌等^[11] 研究了非周期条件下二杂质短聚乙炔中孤子对的性质,并与周期下的某些结果进行了比较,指出链端效应对分子链各种性能必然产生一定影响. 但显然,当分子链足够长时链端效应是可忽略的. 本文将聚乙炔分子链简化成一维 N 格点复式格子模型,在考虑链端效应的情况下,计及电子的非近邻跳跃,数值计算了非周期边界条件下格点数分别等于 $N = 10, 50, 100$ 和 200 的有限系统的能谱,并与周期条件下的结果进行了比较. 结果表明,当格点数 $N \geq 50$ 时,链端效应可忽略,利用周期性边界条件研究导电高分子的电子结构问题是适宜的. 但是理论和实验都表明聚乙炔链的 CH 基团数 $N < 50$,因而系统的边界条件将对其性质起很大作用,此时应充分考虑采用周期性边界条件计算所带来的偏差,这对于了解导电高分子的电子结构具有十分重要的意义.

1 理论方法

将聚乙炔分子简化成一维 N 格点复式晶格模型,并设每个格点有一个 π 电子. 二次量子化形式的系统哈密顿量^[12]

$$H = \sum_{i,j} t_{ij} (a_i^\dagger a_j + a_i^\dagger a_j) \quad (1)$$

式中 $a_j^\dagger$ 是第 j 个格点的电子产生算符, a_i 是第 i 个格点的电子湮灭算符, t_{ij} 表示第 i 个格点的电子到第 j 个格点的电子跳跃积分. 本文仅考虑最

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近邻和次近邻电子跳跃项,于是(1)式可写成:

$$H = \sum_j t_{j,j+1} (a_{j+1}^+ a_j + a_j^+ a_{j+1}) + \sum_j t_{j,j+2} (a_{j+2}^+ a_j + a_j^+ a_{j+2}) \tag{2}$$

上式中 $t_{j,j+1}$ 、 $t_{j,j+2}$ 分别代表碳原子在平衡位置时,最近邻和次近邻的电子跳跃能量.

将(2)式对角化即可求如下久期方程

$$\sum_{j=1}^N c_j (H_{kj} - E \delta_{kj}) = 0 \tag{3}$$

(3)式中的哈密顿矩阵元 $H_{kj} = t_{kj}$,依次考虑最近邻和次近邻.由数值方法可求特征值 E 及特征矢 $|c_j|$.

DOS 随能量的分布曲线可用 δ 函数表示:

$$\rho(E) = 2 \sum_i g_i \delta(E - E_i) \tag{4}$$

$\rho(E)$ 表示态密度,因子 2 表示每一能量状态的两个自旋态, g_i 为能量简并度.实际处理 DOS 图象时,还需对能量作适当的高斯增宽.

2 模型与计算结果

设每个格点有一个 π 电子,可作最近邻跳跃和次近邻跳跃.对于非周期边界条件,如图 1 所示,考虑边缘效应,哈密顿矩阵元为:

最近邻:

$$t_{j,j+1} = \begin{cases} a & (j = 3, 5, 7, \cdots, N-3) \\ b & (j = 2, 4, 6, \cdots, N-2) \\ d & (j = 1, 2, 3, \cdots, N-1) \end{cases} \tag{5}$$

次近邻:

$$t_{j,j+2} = c \quad (j = 1, 2, 3, \cdots, N-2) \tag{6}$$

对于周期边界条件,如图 2 所示,哈密顿矩阵元为:

最近邻:

$$\begin{aligned} t_{j,j+1} &= a \quad (j = 1, 3, 5 \cdots N-1) \\ t_{j,j+1} &= b \quad (j = 2, 4, 6 \cdots N) \end{aligned} \tag{7}$$

次近邻:

$$t_{j,j+2} = c \quad (j = 1, 2, 3, \cdots, N) \tag{8}$$

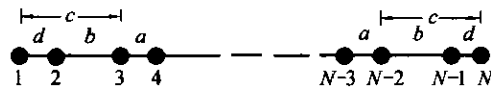


Fig. 1 Aperiodic boundary condition

我们考虑格点数分别为 $N = 10, 50, 100, 200$ 的聚乙炔分子.由于聚乙炔链间耦合较弱,讨论时

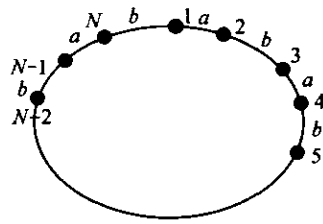


Fig. 2 Periodic boundary condition

可根据实际选取恰当的参数.利用 EMF (The extended Wannier function) 方法,考虑电子的非最近邻跳跃,当畸变振幅为 0.0033 nm 时,通过数值计算得到的结果为^[13], $a = 3.042$ eV, $b = 2.144$ eV, $c = 0.301$ eV,这些电子跳跃积分值相应的能隙为 1.692 eV^[13],与实验值 1.7 eV^[14-17] 符合很好.由于电子的跳跃与格点的畸变振幅有关, a 与 b 之比不是一常数.当畸变振幅固定时, a 与 b 之比基本为一常数.原子轨道指数的改变,对这一比例常数的影响不大,据此我们可设 $a = 1$, $b = 0.705$.对于次近邻跳跃 c ,几乎与畸变振幅无关,但强烈依赖于原子轨道指数的大小.指数小, c 值大.指数大, c 值小,因此这里我们设 $c = 0.1$.非周期性边界条件下边缘处的电子跳跃与中心可能不同,可设边缘的最近邻平均跳跃为 $d = 0.9$.利用数值计算,可分别求出两种边界条件下的能量值,利用(5)式对能量做适当的高斯增宽得到电子态密度(DOS)随能量的分布曲线.相应的带宽、能隙等物理量列于表 1.

2.1 只考虑最近邻的情况

在只考虑最近邻相互作用的情况下,我们计算了在不同的 b, c, d 时,格点数为 $N = 10, 50, 100$ 和 200 的电子态密度(DOS)与能量 E 的关系曲线图,结果见图 3.从图 3 可知,导带和价带是对称的.周期性边界条件下能量发生简并.而非周期边界条件下无此简并,这是由于非周期边界条件其对称性要比周期性边界条件低.我们以 B 表示带宽, EG 表示能隙, C 表示导带宽, V 表示价带宽,只考虑最近邻耦合时两种边界条件下各物理量列于表 1,相对误差列于表 2.由表 2 可知在当前参数下,当 CH 基团数 $N = 10$ 时,由于链端效应,两种边界条件下带宽、能隙等物理量的相对误差较大,当 $N \geq 50$ 时已足够小,当 $N > 200$ 时,两者几乎无差别,表明链端不再起作用.

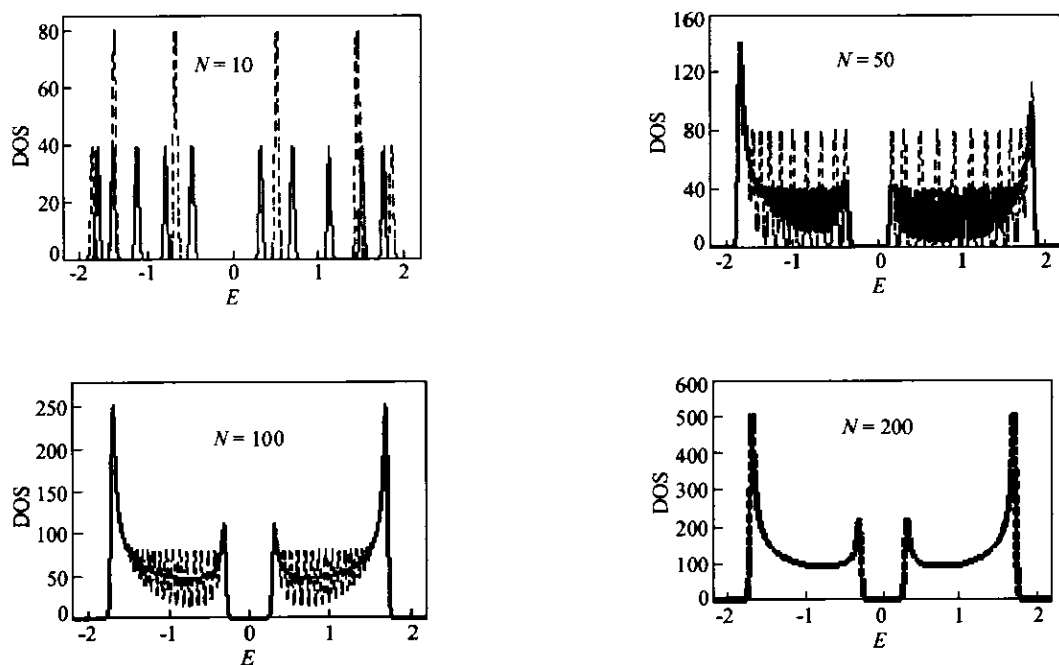


Fig. 3 DOS versus E under two boundary conditions with considering the nearest-neighbor hopping for $N = 10, 50, 100$ and 200

The broken curve represents the periodic boundary condition with $b = 0.705a$, $c = 0$, and the solid curve represents the aperiodic boundary condition with $b = 0.705a$, $c = 0$ and $d = 0.9a$. (The unit of E is a , and the unit of DOS is at discretion.)

2.2 考虑次近邻的情况

当计及次近邻时, 导带和价带不再对称, 从图 4 结果可见, 价带变窄而导带增宽. 价带底部附近的电子态密度随着 N 的增加而显著增加. 导带的

增宽使得电子不易电离, 这就意味着较多电子处于较低的能量状态, 使价带变窄. 另一方面随着 N 的增加, 能隙减少, 分子链的量子尺寸效应减弱.

次近邻时两种边界条件下各物理量列于

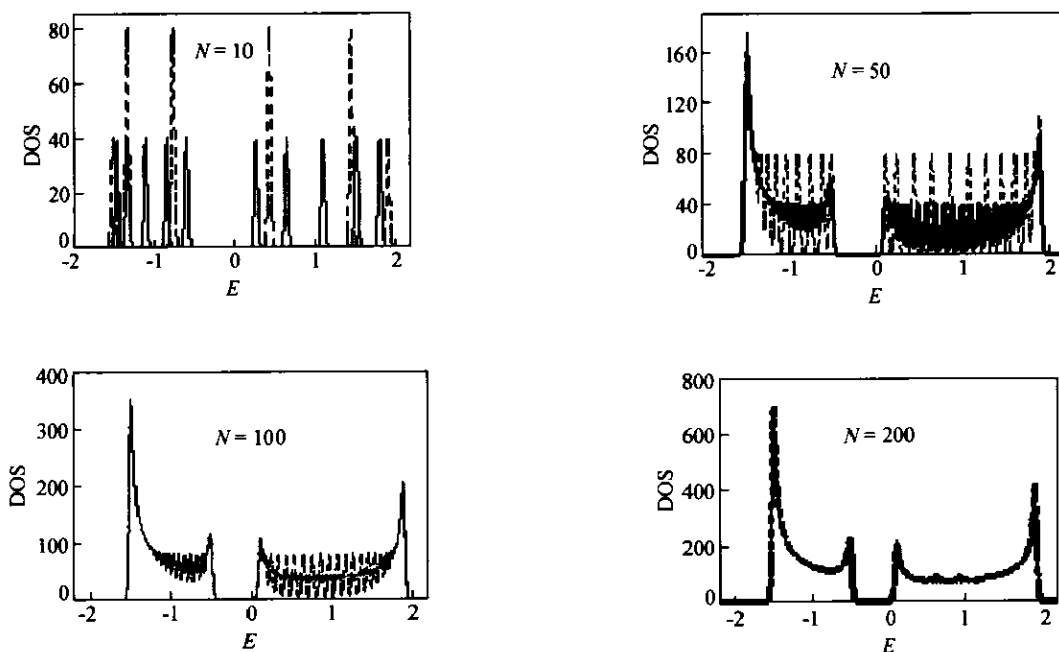


Fig. 4 DOS versus E under two boundary conditions with considering the next-neighbor hopping for $N = 10, 50, 100$ and 200

The broken curve represents the periodic boundary condition with $b = 0.705a$, $c = 0$, and the solid curve represents the aperiodic boundary condition with $b = 0.705a$, $c = 0$ and $d = 0.9a$. (The unit of E is a , and the unit of DOS is at discretion.)

表 1,相对误差列于表 2.由表 2 可知,此时带宽、能隙等物理量的相对误差随 N 的增大而减小,当 N 为 50 以上时已足够小,接近于只考虑最近邻耦合的情况.从表 1 还可看出,对于短链情形,如 $N = 10$ 时,周期条件下能隙值较非周期条件下的为大,且远大于实验值 1.7 eV(相当于 0.559 a),而当 $N \geq 50$,两种边界条件下能隙值与实验值已比较接近.

对于不同的格点畸变振幅及原子轨道指数,参数 a, b, c 值将有所不同.图 5 给出了 $a = 1, b = 0.75, c = 0.05, d = 0.9$ 时两种边界条件下 DOS 曲线,表 1、表 2 分别列出了相应带宽、能隙等各物理量及其相对误差.如非周期条件下边缘

次近邻跳跃与中心有所不同,即次近邻矩阵元 $c' \neq c$,就会使导带宽和价带宽发生变化;与 $c' = c$ 的情况相比, $c' > c$ 时导带增宽而价带变窄, $c' < c$ 时则导带变窄、价带增宽.能隙和带宽受 $c' \neq c$ 的影响是随 N 的增加而减小的,当 $N \geq 50$ 时几乎不受其影响,可不必考虑链端次近邻矩阵元 c' 的不同.图 6 给出了 $a = 1, b = 0.705, c' = 0.05, d = 0.9$ 和 $a = 1, b = 0.705, c' = 0.20, d = 0.9$ 时的 DOS 曲线,并将 $a = 1, b = 0.705, c = 0.1, d = 0.9$ 时的 DOS 曲线画在同一坐标系中以作比较.表 3 和表 4 分别给出了相应各物理量以及与周期条件下($a = 1, b = 0.705, c = 0.1$)对应量的相对误差.

Table 1 The physical quantities of *trans*-polyacetylene under two kinds of boundary conditions with various parameters of hopping for $N = 10, 50, 100$ and 200

Parameter of hopping		Periodic boundary condition			Aperiodic boundary condition		
		$b = 0.705a$		$b = 0.75a$	$b = 0.705a, d = 0.9a$		$b = 0.75a, d = 0.9a$
		$c = 0$	$c = 0.1a$	$c = 0.05a$	$c = 0$	$c = 0.1a$	$c = 0.05a$
$N = 10$	B	3.410	3.410	3.500	3.529	3.260	3.344
	EG	1.194	1.194	1.182	0.858	0.856	0.801
	C	1.108	1.470	1.340	1.201	1.535	1.438
	V	1.108	0.746	0.978	1.201	0.869	1.106
$N = 50$	B	3.410	3.410	3.500	3.404	3.404	3.493
	EG	0.627	0.627	0.545	0.617	0.617	0.533
	C	1.392	1.790	1.677	1.393	1.790	1.678
	V	1.392	0.993	1.278	1.393	0.997	1.282
$N = 100$	B	3.410	3.410	3.500	3.408	3.408	3.498
	EG	0.590	0.590	0.500	0.598	0.598	0.510
	C	1.410	1.810	1.700	1.405	1.804	1.694
	V	1.410	1.010	1.300	1.405	1.006	1.295
$N = 200$	B	3.410	3.410	3.500	3.410	3.410	3.500
	EG	0.590	0.590	0.500	0.592	0.592	0.503
	C	1.410	1.810	1.700	1.409	1.809	1.698
	V	1.410	1.010	1.300	1.409	1.009	1.300

B, EG, C and V represent band width, energy gap, conduction band and valence band of periodic boundary condition, respectively. Here the nearest-neighbor hopping is considered.

Table 2 The relative errors of B, EG, C and V under two kinds of boundary conditions

	Case A				Case B				Case C			
	$N = 10$	$N = 50$	$N = 100$	$N = 200$	$N = 10$	$N = 50$	$N = 100$	$N = 200$	$N = 10$	$N = 50$	$N = 100$	$N = 200$
ΔB	4.43	0.18	0.06	0	4.40	0.18	0.06	0	4.46	0.20	0.06	0
ΔEG	28.1	1.59	1.36	0.34	28.3	1.59	1.36	0.34	32.2	2.20	2.00	0.60
ΔC	8.39	0.07	0.35	0.07	6.73	2.18	1.88	2.10	7.31	0.06	0.35	0.12
ΔV	8.39	0.07	0.35	0.07	12.1	3.63	4.36	4.06	13.1	0.31	0.38	0

Here the nearest-neighbor hopping is considered. $\Delta B, \Delta EG, \Delta C$ and ΔV is the relative error of B, EG, C and V between periodic boundary condition and aperiodic boundary condition, respectively. (Case A: periodic boundary condition with $b = 0.705a, c = 0$; aperiodic condition with $b = 0.705a, c = 0, d = 0.9a$; Case B: periodic boundary condition with $b = 0.705a, c = 0.1a$; aperiodic boundary condition with $b = 0.705a, c = 0.1a, d = 0.9a$; Case C: periodic boundary condition with $b = 0.75a, c = 0.05a$; aperiodic boundary condition: $b = 0.75a, c = 0.05a, d = 0.9a$)

Table 3 The physical quantities of *trans*-polyacetylene under two kinds of boundary conditions with various parameters of hopping for $N = 10, 50, 100$ and 200

N	$b = 0.705a, c' = 0.05a, d = 0.9a$				$b = 0.705a, c' = 0.20a, d = 0.9a$			
	B_p	EG_p	C_p	V_p	B_p	EG_p	C_p	V_p
10	3.259	0.858	1.368	1.034	3.266	0.850	1.870	0.546
50	3.404	0.617	1.591	1.195	3.404	0.617	1.988	0.799
100	3.408	0.598	1.605	1.206	3.408	0.612	1.990	0.807
200	3.410	0.592	1.609	1.209	3.410	0.602	1.998	0.809

B, EG, C and V represent band width, energy gap, conduction band and valence band of periodic boundary condition, respectively. Here the next-neighbor hopping is considered.

Table 4 The relative errors of B, EG, C and V under two kinds of boundary conditions

	Case A				Case B			
	$N = 10$	$N = 50$	$N = 100$	$N = 200$	$N = 10$	$N = 50$	$N = 100$	$N = 200$
ΔB	4.43	0.18	0.06	0	4.22	0.18	0.06	0
ΔEG	28.1	1.59	1.36	0.39	28.8	1.59	3.73	2.03
ΔC	6.94	11.1	11.3	11.1	27.2	11.1	9.94	10.4
ΔV	38.6	20.3	19.4	19.7	26.8	19.5	20.1	19.9

Here the next-neighbor hopping is considered. $\Delta B, \Delta EG, \Delta C$ and ΔV is the relative error of B, EG, C and V between periodic boundary condition and aperiodic boundary condition, respectively. (Case A: periodic boundary condition with $b = 0.705a, c = 0.1a$ and aperiodic condition with $b = 0.705a, c' = 0.05a, d = 0.9a$; Case B: periodic boundary condition with $b = 0.705a, c = 0.1a$ and aperiodic boundary condition with $b = 0.705a, c' = 0.20a, d = 0.9a$.)

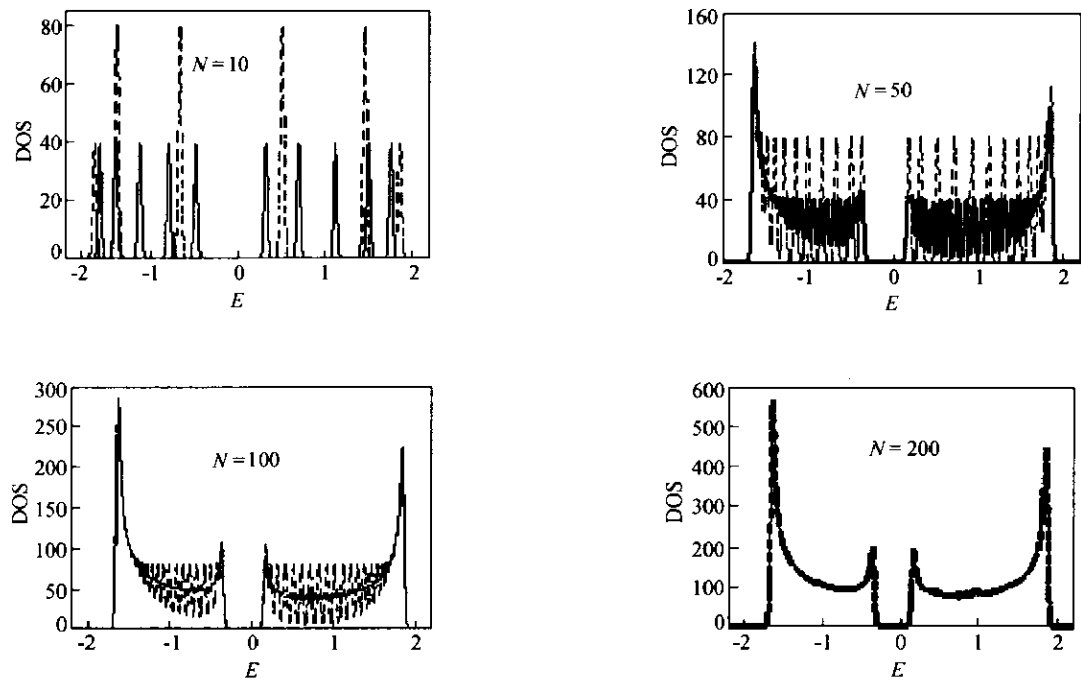


Fig. 5 DOS versus E under two boundary conditions with considering the next-neighbor hopping for $N = 10, 50, 100$ and 200. The broken curve represents the periodic boundary condition with $b = 0.75a, c = 0.05a$, and the solid curve represents the aperiodic boundary condition with $b = 0.75a, c = 0.05a$ and $d = 0.9a$. (The unit of E is a , and the unit of DOS is at discretion.)

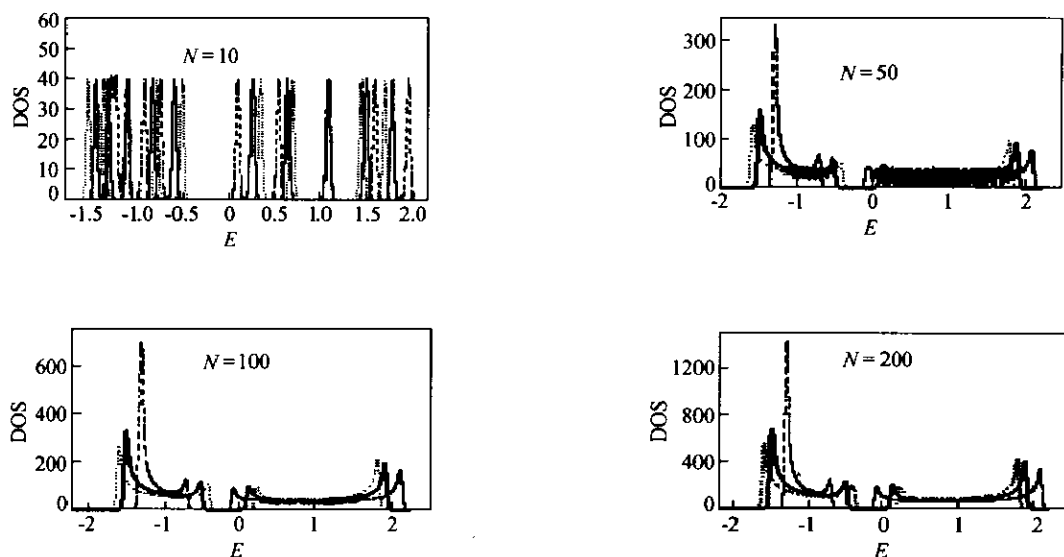


Fig. 6 DOS versus E under different value with considering the next-neighbor hopping for $N = 10, 50, 100$ and 200

The broken curve represents the aperiodic boundary condition with $b = 0.705a$, $c' = 0.2a$, $d = 0.9$; The solid curve represents the aperiodic boundary condition with $b = 0.705a$, $c = 0.10a$, $d = 0.9a$ and the dot curve represents the aperiodic boundary condition with $b = 0.705a$, $c' = 0.05a$ and $d = 0.9a$. (The unit of E is a , the unit of DOS is at discretion.)

本文分别计算了 $N = 10, 50, 100$ 和 200 时, 两种不同边界条件的一维复式有限长链在不同结构参数条件下, π 电子在最近邻及次近邻格点跳跃的态密度, 计算结果表明, (1) 考虑最近邻时, DOS 曲线呈对称分布. 在考虑次近邻耦合时, DOS 对称性被破坏. c 越大即次近邻耦合越强, 导带宽愈大于价带宽, 对称性越差. (2) 当 N 较小时, 在非周期边界条件下考虑链端效应, 出现表面态. 当 N 较大时, 可看出表面态夹杂在价带和导带中不易辨别. 但表面态都面向费米面一侧. (3) N 较小时, 周期边界条件下费米面附近的态密度比非周期边界条件下的大, 价带底部和导带顶部的态密度在两种边界条件下接近相同. N 较大时态密度的大

小和分布在两种边界条件下趋于一致. (4) 随 N 的增加, 两种边界条件的电离能是随 N 减小的. 在同一 N 的情况下, 周期性边界条件的电离能要略大于非周期性的情况. 当 $N < 50$ 时, 这种差别更加明显.

总之, 对于有限长反式聚乙炔链, 我们将其简化成一维复式有限晶格长链, 考虑链端效应. 结果表明, 由于聚乙炔链的 CH 基团数 $N < 50$, 系统的边界将起很大作用, 不宜使用周期性边界条件研究问题. 对于基团数足够大 ($N \geq 50$) 的导电高分子链, 使用周期性边界条件解决类似的有限系统问题是适宜的.

REFERENCES

- 1 Peierls R E. Quantum Theory of Solid. London: Oxford Univ Press, 1955. 38 ~ 126
- 2 Akayama H T, Lin-liu Y R, Maki K. Phys Rev Lett, 1979, 42: 1677 ~ 1680
- 3 Su W P, Schrieffer J R, Heeger A J. Phys Rev Lett, 1979, 42: 1698 ~ 1701
- 4 Heeger A J, Kivelson S, Schrieffer J R, Su W P. Rev Mod Phys, 1988, 60: 781 ~ 798
- 5 Fu R, Shuai Z, Lin J, Sun X, Hicks J C. Phys Rev, 1988, B38: 6298 ~ 6300
- 6 Subbaswamy K R, Grabowski M. Phys Rev, 1981, B24: 2169 ~ 2173
- 7 Hubbard J. Proc R Soc, 1963, A276: 238 ~ 245
- 8 Wu C Q, Sun X. Phys Rev, 1986, B33: 8772 ~ 8775
- 9 Brivio G D, Mulazzi E. Phys Rev, 1984, B30: 876 ~ 882
- 10 Carter P W, Porter J D. Phys Rev, 1991, B43: 14478 ~ 14484
- 11 Sun Guochang (孙国昌), Xie Shijie (解士杰), Mei Liangmo (梅良模). Acta Physica Sinica (物理学报), 1993, 42: 1311 ~ 1316

- 12 Tong Guoping(童国平). Chinese Journal of Atomic and Molecular Physics(原子与分子物理学报), 1996, 13: 195 ~ 202
- 13 Tong Guoping(童国平), Feng Jiaxing(冯家星), Li Henian(李鹤年). Acta Physica Sinica(Overseas Edition), 1995, (4): 285 ~ 291
- 14 Weinberger B R. Phys. Rev. Lett., 1984, 53: 86 ~ 89
- 15 Ma Yongmei(马永梅), Liu Xiaowu(刘小武), Guo Junshi(过俊石), Xie Hongquan(谢洪良). Acta Polymerica Sinica(高分子学报), 1998, (1): 14 ~ 20
- 16 Zhao Yingxi(赵莹歆), Liu Changyan(刘昌炎). Acta Polymerica Sinica(高分子学报), 1999, (3): 373 ~ 376
- 17 Song Yuexian(宋月贤), Wang Hongli(王红理), Zheng Yuansuo(郑元锁), Xu Chuanxiang(徐传铤). Acta Polymerica Sinica(高分子学报), 2002, (1): 92 ~ 95

EFFECTS OF BOUNDARY CONDITIONS ON THE ELECTRON STRUCTURE IN CONDUCTING POLYMERS

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Abstract As the real *trans*-polyacetylene molecule has finite chain length, its chain-terminal effects on various properties should be taken into account, that is to say, the aperiodic boundary condition should be employed in studying the properties of conducting polymers. However, if *trans*-polyacetylene chain is long enough, the chain-terminal effects can be ignored. In this paper, a one-dimensional finite compound lattice model of *trans*-polyacetylene chain is adopted. With considering the chain-terminal effects and the next-neighbor hopping interactions, the energy spectra and the density of states are calculated for *trans*-polyacetylene chains with the lattice number N from 10 to 200 under the periodic and aperiodic boundary conditions. The effects of chain length and interaction parameter on density of states and band width are also discussed. It is shown that the curves of DOS are symmetrical when the nearest-neighbor hopping is merely considered, and the valence and conduction bands are unsymmetrical when the next-neighbor term is taken into account. At the same time, some results under two kinds of boundary conditions are compared. When $N < 50$, the surface states appear under the aperiodic boundary condition, as well as DOS nearby the Fermi surface is larger than that under the periodic boundary condition. When $N \geq 50$, the surface states are difficult to distinguish between the valence and conduction bands, and DOS tends to be identical under two kinds of boundary conditions. Moreover, with N increasing, the difference of ionization energy under the two boundary conditions is reduced for the same parameter. In conclusion, when $N < 50$, there is a large difference for nearest-neighbor hopping and next-neighbor hopping due to the chain-terminal effect. This indicates that the aperiodic boundary condition plays an important role in dealing with finite systems. However, when $N \geq 50$, since the chain-terminal effect can be neglected, the periodic boundary condition is suitable for the finite *trans*-polyacetylene system.

Key words Compound lattice, Density of states, Surface states, Chain-terminal effect