

Charge transfer states in a chain molecule with a dangling bond

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 L285

(<http://iopscience.iop.org/0953-8984/9/19/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 08:38

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

Charge transfer states in a chain molecule with a dangling bond

John P Hernandez

Department of Physics and Astronomy, University of North Carolina,
Chapel Hill, NC 27599-3255, USA

Received 7 April 1997

Abstract. Charge transfer states are considered in chain molecules, such as those of selenium or tellurium, when the molecule has a dangling bond. A simple model for these states, in which the dangling bond becomes negatively charged and the hole is distributed among the lone pair states of the atoms which constitute the chain molecule, is solved. The results should be useful in helping to unravel the structural, thermodynamic, and electronic properties of materials with such molecules.

A unified study is required to understand the electronic, structural and thermodynamic properties of matter. To attempt a microscopic understanding of materials which have the simplest directional bonds, certain electronic states of a model of the constituent structures are considered. The materials of interest are composed of atoms with an electronic configuration of $s^2 p^4$, outside a closed shell; selenium and tellurium are examples of such materials [1, 2, 3]. In a twofold coordinated atom, two of its valence electrons form the covalent bonds with the nearest-neighbour atoms, while its remaining valence electrons occupy a lone pair state and a more deeply bound state. A material in which all atoms were two-fold coordinated would be a semiconductor with the energy gap corresponding to excitation of lone pair electrons to antibonding states.

Alternatives to two-fold coordination are possible. In non-crystalline cases, singly coordinated atoms give rise to dangling bonds, except in the cases of the doubly bonded dimer and closed rings. In a chain of two-fold coordinated atoms, with at least one loose end, electrons from within the chain can charge the dangling bonds. Such electrons will most favourably come from lone pair states and will not be localized within a single site, as such localization would not be an eigenstate of the system unless self-trapping took place. This charge transfer model is implied, apparently as a suspicion, in the recent interpretation of the optical reflectivity of Se–Te alloys [4], on referring to liquid Te. Also, the possibility of charge transfer is raised in a theoretical calculation, by Koslowski [5], of the electronic states of randomly conformed chains of Se atoms. In this latter case, the dangling bonds are said to have unit negative charge with the positive charge being in a bipolaron state (two dangling bonds exist in the 64-atom chains considered, but it is unclear why self-trapping must take place); however, although that work attempts to estimate the electrostatic interaction, it does not calculate it in detail. Finally, in a locally neutral situation, three-fold coordination of an atom would require promotion of a fourth electron to an antibonding state. Based on charged defects, it appears that the most favourable method of achieving three-fold coordination, without occupancy of the antibonding states, is the fusion of a charged dangling bond with the interior of a positive chain, leaving a net positive charge at the junction. Such fusion is

and $r = t_1/(2t)$, the Schrödinger equation is written as follows.

$$(x + V_1/n)\alpha_n = (\alpha_{n-1} + \alpha_{n+1})/2 \quad n > 1 \tag{2a}$$

$$(x + V_1)\alpha_1 = r\alpha_0 + \alpha_2/2 \tag{2b}$$

$$(x + V_0)\alpha_0 = r\alpha_1. \tag{2c}$$

Linearly independent solutions of equation (2a) are the even states obtained previously [8, 9]. Changing variables to z and λ , with $x = (z + z^{-1})/2$ and $V_1 = \lambda(z - z^{-1})/2$, allows the solutions to be written as:

$$\gamma_1(n) = z^{-n+1}\Gamma(n - \lambda)F(1 - n; 1 + \lambda; 1 - n + \lambda; z^2)/[\Gamma(n)\Gamma(1 - \lambda)] \tag{3a}$$

$$\gamma_2(n) = z^n\Gamma(1 - \lambda)\Gamma(1 + n)F(n; -\lambda; 1 + n - \lambda; z^2)/\Gamma(1 - \lambda + n) \quad |z| < 1. \tag{3b}$$

$F(a; b; c; z)$ are the hypergeometric functions and $\Gamma(a)$ are the gamma functions [10]. Then, the α_n in equation (1) can be written as a linear combination of the solutions in equations (3a) and (3b),

$$\alpha_n = \alpha_0[c_1\gamma_1(n) + c_2\gamma_2(n)] \quad n > 0 \tag{4}$$

with coefficients chosen to satisfy equations (2b) and (2c). The constant α_0 is to be determined from the orthonormality of the eigenfunctions.

The bound-state eigenvalues are obtained from the boundary condition requiring that $\alpha_{n \rightarrow \infty}$ vanish. Thus, the coefficients $c_1 = 0$ and $c_2 = (x + V_0)/[r\gamma_2(1)]$, while it is required that

$$I = r^2/(x + V_0). \tag{5}$$

The function I is defined by

$$I \equiv (x + V_1) - [zF(2; -\lambda; 3 - \lambda; z^2)]/[(2 - \lambda)F(1; -\lambda; 2 - \lambda; z^2)]. \tag{6}$$

For these bound states, it is required that $-1 < z < 0$, so that $x < -1$ and $\lambda > 0$. A numerical solution of equation (5) is obtainable as follows. From the definitions, I can be recast as a function of the constant V_1 and the variable λ , by using the relations $z^{\pm 1} = \pm(V_1/\lambda) - [(V_1/\lambda)^2 + 1]^{1/2}$ and $x = -[(V_1/\lambda)^2 + 1]^{1/2}$. Then, it can be verified from equation (6) that $I(\lambda \rightarrow 0^+) \rightarrow -\infty$, since $x \rightarrow -\infty$ and $I \rightarrow (x + V_1) - z/2$. The integer values of $\lambda(= p)$ are poles of both $\gamma_2(1, 2)$, but the poles cancel leaving I well behaved for those parameter values; in fact, $I(\lambda = p > 0) = 0$. Finally, I is continuous except for simple poles at the zeros of $\gamma_2(1)$. The above statements immediately allow bounds to be placed on the eigenvalues. As λ increases from zero, the right hand side of equation (5) decreases (from its zero value at $\lambda = 0$). The ground state eigenvalue must therefore be found within the interval $0 < \lambda < 1$. If $V_0 > [V_1^2 + 1]^{1/2}$, the ground state is lower than in the alternative case since $r^2/(x + V_0)$ will then have a pole for $\lambda < 1$, and this value of λ yields an upper bound to the ground state energy. Thus, for all cases, the ground state energy is lower than all $V(n)$. As far as excited states are concerned, there is another solution to equation (5) in each of the intervals $p < \lambda < p + 1$, for positive integer values of p . As long as $x < -V_0$, an eigenvalue is to be found between each value of λ which correspond to a pole of I and the next higher integer. Once $x > -V_0$, there is an eigenvalue at a smaller λ than each of those for which I has a pole.

As a numerical example, consider the case in which $V_1 = 1.5$, $V_0 = 1.2$ and $r = 0.3789$. The value of V_1 equates $x = -V_0$ with $\lambda = 2.261$. Thus, the signs of the two sides of equation (5) imply that the lowest eigenvalues correspond to the following intervals:

$$\begin{aligned} 0 < \lambda_0 < 1, & & -\infty < x_0 < -1.803 \\ 1.694 < \lambda_1 < 2, & & -1.336 < x_1 < -1.250 \end{aligned}$$

$$2.261 < \lambda_2 < 2.729, \quad -1.20 < x_2 < -1.141$$

$$3 < \lambda_3 < 3.741, \quad -1.118 < x_3 < -1.077$$

and so on. Finally, using the given value of r allows the eigenvalues to be obtained:

$$\lambda_0 = 0.900, \quad x_0 = -1.944$$

$$\lambda_1 = 1.793, \quad x_1 = -1.304$$

$$\lambda_2 = 2.657, \quad x_2 = -1.148$$

$$\lambda_3 = 3.548, \quad x_3 = -1.086$$

and so on. For the ground state, the normalization constant is found to be $\alpha_0 = 0.409$, which allows the charges on the atoms (labelled by n) to be found. In units of the charge on the proton, the atomic charges (q) are as follows.

n	0	1	2	3	4
q	-0.833	+0.644	+0.162	+0.025	+0.003

In this example, C_1^0 is at an energy of $2.4t$ below that of C_1^- ; the energy of the ground state is an additional $1.488t$ lower.

On reconsidering the results, it may not be obvious why the ground state has a value lower than all diagonal elements of the Hamiltonian, the effective potential energy. The reason is clearer when it is recalled that the continuum does not begin at $x = V(\infty) = 0$, but rather at $x = -1$; taking out the highest energy electron results in the lowest energy unbound hole, and a system energy of minus half the lone pair band width. Although such a state need not be lower in energy than $V(0)$, already the continuum begins at an energy below $V(\infty)$. Naturally, it is the possibility of hopping that lowers the energy of any localized, tight-binding state from the value appropriate to its diagonal matrix element.

In real materials there are no isolated, semi-infinite chains, with equally spaced atoms. However, it does not seem possible, for systems with collections of chains longer than a few atoms, that real situations exist which will void the conclusion that a dangling bond must have some negative charge on it. Finite length chains should have some negative charge on both dangling bonds, by symmetry.

To touch on implications of the present result, magnetic and transport results should be reconsidered. For example, data from Warren and Dupree [11], in liquid selenium, were interpreted as giving evidence that, as temperature increases, each chain scission creates two unpaired spins and two neutral dangling bonds. With the present result, unpaired spins do arise from a scission, but the dangling bonds are not neutral. Temperature-dependent average chain lengths and an enthalpy of chain scission were obtained from the temperature dependence of the magnetic properties. Focusing on the results herein, the enthalpy of chain scission is to be apportioned among the breaking of a covalent bond, the quite small mechanical work due to the volume change in forming two chains from one, and the temperature-dependent average Coulomb energy. The apportioning is important, as energies corresponding to covalent bonds in short chains are required to understand, among other things, the chain-dimer equilibrium which is required for calculating the liquid-vapour coexistence. With regards to transport in materials with such chains, high densities of short chains should be the prerequisite for metallic behaviour. The conduction could proceed by hole transport in the lone pair band, from chain to chain, without a requirement that the gap from lone pair states to antibonding ones disappear. However, it is required that the density of available states becomes large enough to overcome localization due to the

disordered potential. The disorder is topological, in the fluid or amorphous solid, and also has contributions due to the charge distribution. That the metallic properties are correlated to a high density of short chains is known, in both fluid selenium and tellurium. That it is most probably due to holes in the lone pair band has been considered, but it was unclear where the electrons, which caused the holes, resided. The present concepts, applied to transport properties, would support interpretations, based on structural studies [2, 3], that metallic conduction in selenium and tellurium fluids does not require three-fold covalent bonding, in contrast to previous speculation [12]. It does require, obviously, that charge may transfer from chain to chain.

References

- [1] Cutler M *Liquid Semiconductors* 1977 (New York: Academic)
- [2] Enderby J E and Barnes A C 1990 *Rep. Prog. Phys.* **53** 85
- [3] Tamura K 1996 *J. Non-Cryst. Sol.* **205–207** 239
- [4] Ikemoto H, Yamamoto I, Tsuzuki T and Endo H 1996 *J. Non-Cryst. Sol.* **205–207** 347
- [5] Koslowski T 1997 *J. Phys.: Condens. Matter* **9** 613
- [6] Anderson P W 1975 *Phys. Rev. Lett.* **34** 953
Street R A and Mott N F 1975 *Phys. Rev. Lett.* **35** 1293
- [7] Kastner M, Adler D and Fritzsche H 1976 *Phys. Rev. Lett.* **37** 1504
- [8] Merrifield R E 1961 *J. Chem. Phys.* **34** 1835
- [9] Hernandez J P and Choi S 1969 *J. Chem. Phys.* **50** 1524
- [10] Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions* (Washington, DC: National Bureau of Standards) pp 556, 255
- [11] Warren W W Jr and Dupree R 1980 *Phys. Rev. B* **22** 2257
- [12] Cabane B and Friedel J 1971 *J. Phys.* **32** 73