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Relationes

Some Comments on the Band Structure Calculations of Linear Chains in the Semiempirical SCF LCAO Crystal Orbital Approximation

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The semiempirical SCF LCAO crystal orbital method was formulated for arbitrary solids in the nearest neighbour approximation in a previous paper [*1*]. This method working with complex matrices may be applied in the case of arbitrary number of atoms in the elementary cell (a recent application was performed for different homopolynucleotide chains [*2*]). The mentioned approximation takes into account both the resonance (β) and coulomb (γ) integrals only between nearest neighbours. This approximation is justified for the β integrals which decrease exponentially with distance. This, however, is not the case of the γ integrals. If we assume for them the usual $1/R$ dependence and sum these integrals for the whole infinite chain (all neighbours approximation) we obtain, as it is well known, a logarithmic divergence.

The purpose of this comment is to show that if we take into account also the dependence of bond orders on the distance in the case of a linear chain containing only one atom in the elementary cell, the mentioned divergence does not occur. This result holds for any value of the wave number k (including the delicate value $k = 0$).

In the P-P-P approximation we may write the element of the matrix F, which provides in the case studied, the different SCF one-electron levels within the band, if we use for the β integrals the first neighbour approximation and for the γ integrals the all neighbours approximation, as follows:

$$F(k) = 2\beta \cos k - \sum_{l=1}^{\infty} p^{(l)} \gamma^{(l)} \cos kl + C\,, \tag{1}$$

where we take for the coulomb integrals between l-th neighbours

$$\gamma^{(l)} = \frac{1}{l} \tag{2}$$

and $p^{(l)}$ denotes the bond order between atoms belonging to elementary cells which are from each other in the distance l (we use throughout this paper as distance unit the distance between neighbouring cells).

In the case of one atom in the elementary cell $p^{(l)}$ is defined as

$$p^{(l)} = \frac{1}{\pi} \int_{-\pi/2}^{\pi/2} e^{ikl}\, dk = \frac{2}{\pi l} \sin \frac{\pi l}{2} . \tag{3}$$

[Eq. (3) gives in the limiting case $l = 0$ the charge density equal to one. Further we have denoted in Eq. (1) the k-independent part of $F(k)$ by C].

Thus we have to deal only with the series

$$- \sum_{l=1} p^{(l)}\, \gamma^{(l)} \cos kl = - \frac{2}{\pi} \sum_{n=0}^{\infty} (-1)^n \frac{\cos [(2n+1)\, k]}{(2n+1)^2} , \tag{4}$$

which we obtain if we substitute both (2) and (3) in the left hand side of the Eq. (1). In order to calculate the value of this convergent series let us apply the well known identity

$$\tfrac{1}{2} \lg \operatorname{tg} \frac{x}{2} = - \sum_{n=0}^{\infty} \frac{\cos [(2n+1)\, x]}{2n+1} . \tag{5}$$

Integrating both sides of (5) we obtain

$$\tfrac{1}{2} \int_0^x \lg \operatorname{tg} \frac{y}{2}\, dy = - \sum_{n=0}^{\infty} \frac{\sin [(2n+1)\, x]}{(2n+1)^2} . \tag{6}$$

Substituting $x = \pi/2 - k$ we get for the series (4) the expression

$$\sum_{l=1}^{\infty} p^{(l)} \gamma^{(l)} \cos kl = \frac{1}{\pi} \int_0^x \lg \operatorname{tg} \frac{y}{2}\, dy = \frac{1}{\pi} I . \tag{7}$$

The improper integral occurring in the right hand side of (7) may be transformed to the form

$$I = \int_0^x \lg y\, dy + \int_0^x \lg \left(\frac{\operatorname{tg} \frac{y}{2}}{y} \right) dy = I_1 + I_2 \tag{8}$$

I_1 equals

$$I_1 = x \lg x - x , \qquad \lim_{x \to 0} I_1 = 0 \tag{9}$$

and the proper second integral already can be treated by numerical methods.

Using expression (9) of integral I_1 and performing numerical integration for I_2 we obtain the value of investigated series (4) for different values of k. The results are given in the Table.

Table

k	$1/\pi\, I$
0°	−0.58
15°	−0.57
30°	−0.54
45°	−0.48
60°	−0.39
75°	−0.25
90°	−0.00

Since the bond orders decrease — according to all experiences — with the distance, we may expect that in general case (when we have arbitrary number of atoms within the elementary cell) the occurring expressions, which are similar to the left side of Eq. (4), will be also convergent. Further studies are in progress to prove this expectation.

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References

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