A Modified Coupled-Cluster Based Investigation of Delocalization in Tight-Binding Hamiltonians

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Abstract. – The nature of delocalization in a 1D system ruled by a tight-binding Hamiltonian is investigated. Using a local evaluation of the ground state energy, it is shown that the range of the delocalization effects is rather limited. The method is applied to 1/2 and 1/4 filled systems.

Introduction. – For the last few decades, physicists and chemists have put a lot of effort into understanding the properties of low-dimensional compounds [1–3]. A major achievement was the elucidation of the physical properties of polyacetylene the simplest linear polymer [4]. Since then, a large number of inorganic chains have been subject to extensive studies. Usually the chemically relevant and extremely simple model Hamiltonian, the Hückel Hamiltonian, has been called for [5–7]. The use of more sophisticated Hamiltonians such as the Hubbard Hamiltonian led to fundamental issues since exact solutions are known for one dimensional systems only [8]. The traditional solid-state picture gives a privilege to delocalization, presented as a collective phenomenon. However, it is known from the solid state and the surface bonding that the local interactions (i.e. bonds) play a dominant role and contain a large part of the chemical actions [6, 9]. Following this trend, we have recently demonstrated that a localized description of the physics of a system ruled by very short-range interactions (i.e. Hückel Hamiltonian) is relevant [10, 11]. Indeed, starting from strongly localized N-electron functions built from either pure Atomic Orbitals (AOs) or fully localized bond Molecular Orbitals (MOs), it is possible to get very good evaluations of the ground state energy of a periodic lattice without any computational effort. The method consists in a self-consistent (SC) perturbation of a zeroth-order wave-function which incorporates high order effects and offers particular convergence properties. The charge transfer contributions are explicitly evaluated, a noticeable difference with the original moments method [13] which focuses on the charge densities. This modified coupled-cluster approach has shed the light on the crucial importance of the local effects which appear to be the quantitatively dominating driving forces responsible for the bond alternation in 1/2 filled conjugated hydrocarbons (i.e. Peierls distortion [12]). The short and medium-range character of delocalization in the ground state clearly appeared

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to be dominant. However, our evaluations based either on pure AOs or bond MOs did not allow one to perfectly reproduce the reference tight-binding calculations. Thus, to which extent delocalization has to be incorporated remains a challenging issue in the study of delocalized systems. Besides, the accurate determination of the low-energy physics of such systems by rather local methods is tempting since it opens the possibility to determine the ground state energy of systems ruled by a variety of model Hamiltonians with an efficient and unexpensive method.

In this paper, we shall first briefly recall the method which has been recently proposed by introducing the so-called set of self-consistent coupled equations (SCPEs) [10]. We will then follow two different strategies based on this method. The first one consists in using MOs delocalized over four-site units, i.e. butadiene MOs, to build the zeroth-order wave-function. The second aims to extend the variational space which had been limited to single charge transfer amplitudes [10, 11]. Higher order terms were incorporated by means of perturbation theory. Thus, starting from a zeroth-order wave-function based either on AOs or MOs, single and double charge transfers as well as second-nearest neighbour charge transfers coefficients will be treated self-consistently. For a strictly non-interacting electron system (i.e. Hückel Hamiltonian), our goal is i) to look into the benefit of both approaches in the evaluation of the ground state energy of a 1/2-filled homogeneous chain, ii) to extract an estimation of the relevant delocalization range, and iii) to investigate the reliability of such local evaluations for 1/4-filled systems. We believe that in the study of periodic lattices, local pictures are very valuable since the information they convey is very instructive in the understanding of bond formation analysis.

**Self-Consistent Perturbation Method.** – Let us consider the Hückel Hamiltonian $H = \sum t(a_{2i-1}^\dagger a_{2i} + a_{2i}^\dagger a_{2i-1})$ ruling an infinite chain of singly occupied valence orbitals. The nearest-neighbour interaction is determined by the hopping integral $t$. The derivation of the Hückel energy for such 1/2-filled system is very standard and leads to $4/\pi \approx 1.273$ in the unit of $t$ [7]. The basic idea behind the SCPEs method is to set the electrons in strongly localized mono-electronic functions $\varphi_i$ to build a $N$-electron zeroth-order determinant $\Phi_0$. Since the $\alpha$ and $\beta$ electrons move independently, one may pair the electrons on the odd sites to give rise to an Atomic Charge Density Wave (ACDW) $\Phi_0 = |\varphi_{2i-1}\varphi_{2i-1}|$. One may as well start from the bond MOs to describe a zeroth-order Bond Density Wave (BDW) determinant. Using the so-called intermediate normalization, the wave-function is expanded in terms of the charge transfer determinants $\{\Phi_k\}$,

$$\Psi = \Phi_0 + \sum_{k \neq 0} c_k \Phi_k \quad (1)$$

As in Ref. [10], we define the first generation subspace $S_1$ as the determinants $\{\Phi_k\}_{k \neq 0}$ which interact with $\Phi_0$ (i.e. $\langle \Phi_0 | H | \Phi_k \rangle \neq 0$). Such determinants $\{\Phi_k\}_{k \neq 0}$ are obtained through charge transfers $T_k^\dagger$ between adjacent units. One can easily show that the cohesive energy $E_{coh}$ is completely determined by the knowledge of the $S_1$ determinants amplitudes, $E_{coh} = H_{00} + \sum_{t \neq 0} c_t H_{0t}$. Let us briefly recall the derivation of the SCPEs starting from the eigen-equation for the $\Phi_k$ determinant :

$$\left( H_{kk} - E \right) c_k + H_{k0} + \sum_{l \neq k} H_{kl} c_l + \sum_\alpha H_{k\alpha} c_\alpha = 0 \quad (2)$$

where the determinants $\alpha$ belong to the higher generation subspaces. If the $\Psi$ expansion is limited to $S_2$-determinants, the $\{c_\alpha\}$ coefficients are determined by means of second-order
perturbation theory. The $\Phi_\alpha$ can be generated from $\Phi_k$ by either the action of a similar $T^\dagger_l$ operation or an operation $R^\dagger_m$ which does not act on $\Phi_0$. The amplitude of the former may depend not only on the $c_k c_l$ product associated with the $T^\dagger_l T^\dagger_m$ parent action on $\Phi_0$ but also on the $c_m c_n$ products such that $T^\dagger_l T^\dagger_m = T^\dagger_m T^\dagger_l$. Let us mention that a major difference with the traditional coupled-cluster approach [14] lies in the participation of the $R^\dagger_m$ operators, the role of which has been recently investigated by means of a block-correlated coupled-cluster formalism [15]. The derivation of the second-order amplitudes has been given previously [10] and leads to:

$$c_\alpha = c_k c_l \frac{\Delta E'_k + \Delta E'_l}{\Delta E_{k+l}} + \sum_{\langle m, n \rangle \neq \langle k, l \rangle} c_m c_n \frac{\Delta E'_{m} + \Delta E'_{n}}{\Delta E_{k+l}}$$  \hspace{1cm} (3)

where the excitation energies $\Delta E_k = H_{kk} - H_{00}$ are shifted by the EPV (Exclusion Principle Violating [16]) correction to deal with higher order corrections [17]:

$$\Delta E'_k = \Delta E_k - EPV(k) = \Delta E_k - \sum_{l, T^\dagger_l \Phi_k=0} H_{0l} c_l$$  \hspace{1cm} (4)

Let us mention that for $\Phi_\alpha$ determinants being generated by a single pair $T^\dagger_l T^\dagger_m$ the additivity in the excitation energies reduces $c_\alpha$ to the simple product $c_k c_l$, resulting in a perfect cancelation of the $c_k c_l H_{0l}$ term in eq. 2. Such situation is likely to occur for remote excitations $T^\dagger_l$ and $T^\dagger_m$, as expected from simple physical considerations.

The $R^\dagger_m T^\dagger_k \Phi_0$ determinants amplitudes can be immediately evaluated from second-order perturbation theory:

$$c_\beta = \sum_n \frac{H_{2n}}{\Delta E'_\beta} e^n$$  \hspace{1cm} (5)

Finally, the SCPEs in terms of the $\{c_k\}_{k \neq 0}$ are derived from eq. 2 by expliciting the coefficients $c_\alpha$ using eqs. 3 and 4. Let us mention that the dimension of the set of coupled equations is equal to the number of charge transfer types in the system.

Part of the present work consists in a SC evaluation of the previous $c_\alpha$ and $c_\beta$ coefficients.

**Extension of the Method.** For a homogeneous periodic lattice, the cohesive energy $E_{coh}$ has been previously evaluated with absolute relative errors 2.6% and 1.5% using AOs or bond MOs, respectively [10]. Thus, it was rather challenging to start with larger units built on the butadiene MOs (four-site MOs) to investigate the importance of the collective effects. In order to clarify the presentation, the strategy will be referred to as $l, L$ where $l$ stands for the size of the building blocks (1, 2 or 4) and $L$ for the extent of the SC treatment. $L = II$ indicates that the $S_1$ and $S_2$ non-factorizable determinants amplitudes are treated in SC way.

In using four-site MOs, the amount of delocalization in the zeroth-order wave-function $\Phi_0$ is enhanced as compared to bond MOs. Thus, one may expect to improve the cohesive energy evaluation. The derivation of the Hückel energies $\{\epsilon_n\}_{n=1-4}$ and MOs coefficients of butadiene is very standard [7]. Let us write $\{i_n\}_{n=1-4}$ the MOs localized on the $i^{th}$ tetrameric unit associated with energies $\{\epsilon_n\}_{n=1-4}$. The energy per atom corresponding to the zeroth-order determinant $\Phi_0 = \{|i_1 i_2 i_2 i_2\}$ reads $E_0/t = (2\epsilon_1 + 2\epsilon_2)/4t = \sqrt{5}/2 \approx 1.118$. Starting from $\Phi_0$, one can generate the $S_1$-subspace. Since the left and right charge transfer absolute amplitudes between adjacent tetrameric units are equal, only four types are to be
considered, namely $c_1 = c_{i_1 \rightarrow j_3}$, $c_2 = c_{i_2 \rightarrow j_4}$, $c'_1 = c_{i_2 \rightarrow j_3}$ and $c'_2 = c_{i_2 \rightarrow j_4}$. As mentioned before, the $\alpha$ and $\beta$ electrons can be treated independently in the Hückel framework (i.e. $E_\alpha = E_\beta = 1/2E_{coh}$). Therefore, the cohesive energy reads:

$$E_{coh} = E_0 + (4c_1 t_1 + 4c_2 t_2 + 4c'_1 t'_1 + 4c'_2 t'_2)/4$$

Using the expressions of the butadiene MOs in terms of the AOs, one immediately finds the coupling matrix elements $t_1 = -t'_2 = 0.224t$, $t'_1 = -0.362t$ and $t_2 = 0.138t$. The generation of the $S_2$-subspace is straightforward but somehow lengthy and will not be fully detailed here. However, the three types of determinants belonging to $S_2$ are shown in fig. 1. The first one corresponds to a double charge transfer generated by a single pair $\{T_k^\dagger, T_l^\dagger\}$. Conversely, the second exemplifies the multiple generation of a double charge transfer (see eq. 3). Finally, the third one gives rise to contributions evaluated by eq. 5. The derivation of the SCPEs for a $1/4$-filled system follows exactly the same pattern by taking the inventory of the different $S_1$ and $S_2$-subspaces determinants. For both fillings, the determination of the nearest-neighbour charge transfer amplitudes implies up to four butadiene units, that is 26 AOs, without eliminating the translational property of the chain.

Instead of increasing the degrees of freedom one can extend the SC treatment. Thus, the second strategy we considered is based on an enlargement of the variational space by treating the $S_1$ and non-factorizable $S_2$ determinants amplitudes $c$ and $d$ in a SC way. Third-order terms are then evaluated from perturbation theory. As a zeroth-order wave-function, we first used the strongly localized determinant built on the AOs. The $S_2$-subspace consists of the double charge transfers $\Phi_{i+j}$ which cannot be factorized as product of simple charge transfers (see fig. 2).

The eigen-equation for the $S_1$ determinants $\Phi_i$ is easily derived:

$$(-3ct) c + t + 2t(d - c^2) = 0$$
Starting from the $S_2$ determinants $\Phi_{i+j}$, the adjacent excitation $T_k^\dagger$ gives rise to a charge transfer $\Phi_\beta$ (see fig. 2) with amplitude $c_\beta$. A third-order expansion gives:

$$c_\beta = -d \left[ H_{k\beta} / \Delta E_0 \right] = cd [3ct/7ct]$$

However, $\Phi_\beta$ can be generated by two other routes. The first one which has the same amplitude $c_\beta$ results from the action of $T_i^\dagger$ on $\Phi_{j+k}$. One can also start from the strictly additive double excitation $T_k^\dagger T_i^\dagger$ (i.e. $c^2$ amplitude) and then propagate an electron along the $j$ bond through $T_j^\dagger$. The resulting contribution is $(3ct/7ct)c^3$. Then, one has to consider the action of $R_i^\dagger$ on $\Phi_{i+j}$ (eq. 2) which generates a third-order determinant $\Phi_\gamma$ (see fig. 2) with amplitude $dt/4ct$ (eq. 5). Remembering that $\Phi_{i+j}$ is directly coupled to the $S_1$ determinants $\Phi_i$ and $\Phi_j$, the second eigen-equation reads:

$$(-5ct)d + 2ct + 2t \left[ (3ct/7ct) (2c^3 + cd) - cd \right] + t [dt/4ct] = 0 \quad (7)$$

whilst the cohesive energy $2ct$ is fully determined by $c$. In the following, eqs. 6 and 7 are referred to as extended SCPEs.

In order to get a clearer understanding of the role of the $R_m^\dagger$ operators, one can finally start from a bond MOs zeroth-order wave-function $\Phi_0$ and use a similar second generation logic to evaluate the cohesive energy $(1 + c)t$. It has been previously observed that the deviation from non additivity is negligible. Thus, the double charge transfer $\Phi_{i,j^*,k^*}$ amplitudes (see fig. 3) can be approximated by $c^2$. However, the $R_m^\dagger$ operators give rise to second-nearest neighbour charge transfer $\Phi_{ik^*}$ (see fig. 3) the amplitudes of which $d$ are self-consistently calculated. Along this framework, the third-nearest neighbour charge transfer $\Phi_{ij^*,k^*}$ amplitudes are estimated from perturbation theory. Such strategy combines the use of intermediate fragments size (bond MOs) and an extension of the SC treatment. The extended SCPEs are very easily derived in terms of the first and second nearest-neighbour charge transfers $c$ and $d$, respectively.

![Fig. 3 – Charge transfers generation using the bond MOs based zeroth-order determinant.](image)

For both strategies, the non-linear set of coupled equations is solved without any computational effort. The cohesive energies for 1/2-filled systems are summarized in Table I. These energies are compared to the ones of finite size clusters $E_{coh}^{(n)}$, the extensions of which $n$ are measured by the number of AOs implied in our approach.

First, using the four-site based determinant, our local evaluation is in excellent agreement with the reference value since it deviates by less than 0.02%. The extended SCPEs strategy starting from the AO determinant (i.e. $(l, L) = (1, II)$) leads to a poorer, still satisfactory, estimation of the cohesive energy. One should note that the delocalization effects are smaller since the local evaluation is limited to 6 lattice parameters. Conversely, the combination of fragment of intermediate size (bond MOs) and an extended SC treatment (i.e. $(l, L) = (2, II)$) displays excellent agreement with the exact value and rather inexpensive cost. Therefore, considering the perturbative treatment which incorporates high-order effects through the EPV corrections, we may conclude that the delocalization effects are effective up to roughly 10
Number of sites 1 2 4

| Extent of the | I    | SC-treatment | II   |
|---------------|------|--------------|------|
| 1.240         | a    | 1.253        | a    |
| (1.205(10))   |      | (1.224(14))  |      |
| 1.273         | (1.246(26)) |    |      |

Table I – Cohesive energy evaluations for a 1/2-filled system ($E_{\text{exact}} = 1.273$). The exponents indicate the number of AOs used in the finite size clusters calculations given in parenthesis. Ref. [10].

lattice parameters. The benefit of our approach which explicitly includes the translational symmetry is significant as seen from the finite size clusters calculations (Table II). Second, inspection of the different contributions to the cohesive energy shows that a major part can be attributed to the $R_{n}^{1}$ excitations which are not active in a strict coupled-cluster formalism. Indeed, if one sets these terms to zero in the SCPEs, the relative error deteriorates (0.02% → 1.6%). The comparison between the SCPEs (2, I) and the extended SCPEs (1, II) strategies is very instructive. Indeed, the numbers of AOs implied are very similar. However, the use of a larger variational space in the extended SCPEs noticeably enhances the accuracy (1.5% → 0.5%). Interestingly, the $d/c^2$ ratio is $\approx 1.253$ whereas based on the bond MOs, the deviation from additivity of the local charge transfers is measured by the EPV corrected excitation energies ratio, that is $\frac{(3ct+3ct)}{5ct} = 1.2$ [10]. Thus, using the extended SCPEs the interference between local excitations is somehow increased and a better estimation results. Similarly, inspection of the second-nearest neighbor charge transfer amplitudes shows that their contribution is significantly enhanced ($d = 0.155$) as compared to the original first generation approach ($d = 2c(2t/2)/(2t + 3ct/2) = c/(2 + 3/2c) = 0.106$) [10].

A very similar approach was applied to a 1/4-filled system. Starting from two-site or four-site MOs, the local evaluations deviate from the exact value (0.900) by 2.9% (0.874) and 0.55% (0.895), respectively. Even though a relative agreement with the reference exact value is reached, the errors are somehow larger. From band structure calculations, it is known that the higher the energy in the dispersion curve, the more numerous the nodes in the orbital. Thus, we may argue that 1/4-filled systems are more delocalized than 1/2-filled ones. The accuracy of our approach which introduces only short-range delocalization effects clearly follows the delocalization nature of the system. However, the extended SCPEs method still leads to a more accurate estimation of the 1/4-filled system energy (0.895) than the one obtained from a 26 AO cluster (0.831).

Conclusions. – In summary, the method we used allowed us to investigate the delocalization effects in a 1D-chain. We showed that the latter are limited since excellent evaluations for both 1/4 and 1/2 filled systems can be obtained from rather local evaluations. Besides, the method offers a way to estimate the delocalization range by step by step incorporating the short and medium range contributions. Beyond roughly a 10-lattice parameter distance, their importance is vanishingly small. From a conceptual point a view, the original SCPEs approach [10] can be developed at will by including higher order terms in the variational space. Such strategy is very powerful since the benefit in terms of accuracy is significant whilst the SCPEs are easily derived. In the view of our results, we believe that the description of important heteroatomic $(AA')_{n}$ chains which are more localized by essence would not be of great interest since the bond MOs description has already produced very satisfactory estimations [10]. However, the methodology can be easily extended to more sophisticated Hamiltonians, including for instance one-site $U$ and inter-site $V$ repulsions, the resolutions of which are traditionally derived from expensive approaches.
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