

# Multireference configuration interaction treatment of excited-state electron correlation in periodic systems: the band structure of *trans*-polyacetylene

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## Abstract

A systematic method to account for electron correlation in periodic systems which can predict quantitatively correct band structures of non-conducting solids from first principles is presented. Using localized Hartree–Fock orbitals (both occupied and virtual ones), an effective Hamiltonian is built up whose matrix elements can easily be transferred from finite to infinite systems. To describe the correlation effects wave-function-based multireference configuration interaction (MRCI) calculations with singly and doubly excited configurations are performed. This way it is possible to generate, both, valence and conduction bands with all correlation effects taken into account. *trans*-polyacetylene is chosen as a test system.

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## 1. Introduction

Recently, with the rapid progress in computing facilities, rather sophisticated numerical methods started to arise which attempt to determine quantitatively correct electronic band structures of solids from first principles. These methods can be grouped in two families: those focusing on ground-state properties such as the electron density (or the quasi-particle Green function) and those trying to approach the full many-body electron wave function.

As a rule, traditional density functional methods are used in solid state physics to study the electronic properties of infinite periodic systems, but since these approaches are not designed for excited states they usually strongly underestimate the band gaps of non-conducting systems. Also these methods do in general not allow improvements in some controlled way.

On the other hand, methods based on many-body wave functions of finite systems are well-established in quantum chemistry. They usually start from an approximate wave function (e.g. the Hartree–Fock (HF) wave function) and approach the correct solution by improving the wave function systematically. The development of such methods for solids only started recently (see below). The band gaps obtained on the HF level (via Koopmans' theorem) are usually far too large, but the situation improves steadily upon successive inclusion of correlation effects. In this sense the wave-function-based methods are more general though more demanding in predicting quantitatively correct electronic structures of periodic system than the common density functional methods.

Among the recently developed wave-function-based approaches to correlated band structures one can distinguish those which employ local Hamiltonian matrix elements in real space [1–4], those which work directly in *k*-space and use many-body perturbation theory to account for electron correlation [5,6], and those which

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use an approximate Green function formalism [4,7,8]. Other approaches to electron correlation in solids [9,10] are presently implemented, corroborating the currently high interest in this new and rapidly growing research field.

The aim of this Letter is to present the local Hamiltonian method which originates from the approach to valence bands described in [1–3] but which can now also treat conduction bands and thus allows to predict *complete* band structures (and in particular band gaps) of non-conducting systems with controlled accuracy. The presented method is designed to be used with any suitable standard quantum-chemical program package. We decided for the multireference version of the single and double configuration interaction method (MRCI(SD)) to account for electron correlation in both the ground and excited states of the system together with a special size-consistency correction we have developed for that purpose [11]. This explicitly includes up to five-particle configurations (three holes and two electrons or vice versa) and therefore goes far beyond any of the other wave-function-based methods mentioned above.

To achieve our goal, the original problem of determining delocalized electronic states with a crystal momentum (Bloch states) is reformulated in terms of localized orbitals in real space (Wannier functions). In this representation one can take advantage of the predominantly local character of correlation effects and evaluate them step-by-step in finite clusters of the periodic system. The approach is purely *ab initio*. We adopt the experimentally known geometry of our test system (*trans*-polyacetylene) and we do not make any approximation for the electron–electron or electron–nuclear interaction.

## 2. The method

The valence band energies  $\varepsilon_{kv}$  of a periodic system are defined as

$$-\varepsilon_{kv} = \text{IP}_{kv} = E_{kv}^{N-1} - E_0^N, \quad (1)$$

where  $E_0^N$  is the ground-state energy of the neutral  $N$ -electron system and  $E_{kv}^{N-1} = \langle \Psi_{kv\sigma}^{N-1} | H | \Psi_{kv\sigma}^{N-1} \rangle$  is the energy of that excited state  $\Psi_{kv\sigma}^{N-1}$  of the  $(N-1)$ -electron system which corresponds to a quasi-hole of spin  $-\sigma$ , crystal momentum  $-\mathbf{k}$  and valence band index  $v$ . The corresponding equation for the conduction band energies  $\varepsilon_{k\mu}$  reads

$$-\varepsilon_{k\mu} = \text{EA}_{k\mu} = E_0^N - E_{k\mu}^{N+1} \quad (2)$$

with  $\mu$  labeling the conduction bands and  $E_{k\mu}^{N+1} = \langle \Psi_{k\mu\sigma}^{N+1} | H | \Psi_{k\mu\sigma}^{N+1} \rangle$  referring to the excited-state of the  $(N+1)$ -electron system which is associated with a quasi-particle of spin  $\sigma$  in a virtual Bloch orbital  $\varphi_{k\mu}$ .

Note, that the band energies are differences of *total* energies rather than simple one-particle energies. Also note, that excited states which do not have any counter part in the single-orbital picture such as satellite and shake-up states are explicitly excluded here.

On the Hartree–Fock level the ground-state wave function of the neutral system is approximated by a single Slater determinant  $\Phi$ , and because in infinite systems there is no orbital relaxation upon removal or adjunct of a single electron, Koopmans’ theorem holds such that the excited states of the  $(N \pm 1)$ -electron system are simply given by

$$|\Phi_{kv\sigma}^{N-1}\rangle = c_{kv\sigma}|\Phi\rangle \quad \text{and} \quad |\Phi_{k\mu\sigma}^{N+1}\rangle = c_{k\mu\sigma}^\dagger|\Phi\rangle. \quad (3)$$

Here,  $c_{kv\sigma}$  and  $c_{k\mu\sigma}^\dagger$  annihilate or create an electron in the respective HF spin orbitals which we obtained directly (together with the HF band energies) from CRYSTAL [12], a standard HF program package for periodic systems.

Applying separate multi-band Wannier transformations to the occupied and virtual Bloch orbitals provides two sets of local Wannier functions,  $\varphi_{Rn}$  and  $\varphi_{Rm}$ , where  $\mathbf{R}$  denotes the lattice vector to the unit cell associated with each Wannier function (see Fig. 1). Using these Wannier functions so-called local one-particle configurations

$$|\Phi_{Rn\sigma}^{N-1}\rangle = c_{Rn\sigma}|\Phi\rangle \quad \text{and} \quad |\Phi_{Rm\sigma}^{N+1}\rangle = c_{Rm\sigma}^\dagger|\Phi\rangle \quad (4)$$

can be introduced, where  $c_{Rn\sigma}$  and  $c_{Rm\sigma}^\dagger$  annihilate or create an electron in the respective Wannier spin orbital. Having switched to the local configurations the Hartree–Fock band energies can be recovered by diagonalizing the  $k$ -dependent ‘ionization potential’ and ‘electron affinity’ matrices,

$$\text{IP}_{mn'}^{\text{HF}}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \text{IP}_{mn'}^{\text{HF}}(\mathbf{R}) \quad \text{with} \quad (5)$$

$$\text{IP}_{mn'}^{\text{HF}}(\mathbf{R}) = \langle \Phi_{0n\sigma}^{N-1} | H | \Phi_{Rn'\sigma}^{N-1} \rangle - E_0^N \delta_{0\mathbf{R}} \delta_{nn'}$$

and

$$\text{EA}_{mm'}^{\text{HF}}(\mathbf{k}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \text{EA}_{mm'}^{\text{HF}}(\mathbf{R}) \quad \text{with} \quad (6)$$

$$\text{EA}_{mm'}^{\text{HF}}(\mathbf{R}) = E_0^N \delta_{0\mathbf{R}} \delta_{mm'} - \langle \Phi_{0m\sigma}^{N+1} | H | \Phi_{Rm'\sigma}^{N+1} \rangle.$$

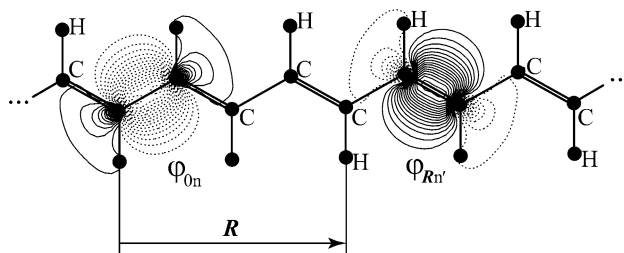


Fig. 1. Two typical local orbitals in *trans*-polyacetylene. Contours are in steps of 0.025 au.

The same holds for the *correlated* band energies provided the Wannier transformations which mediates between the Bloch and the Wannier orbitals is applied to the excited-state wave functions as well, yielding

$$\Psi_{k\nu\sigma}^{N-1} = \sum_n U_{\nu n}(\mathbf{k}) \sum_{\mathbf{R}} e^{-i\mathbf{k}\mathbf{R}} \Psi_{\mathbf{R}n\sigma}^{N-1} \quad \text{and} \quad (7)$$

$$\Psi_{k\mu\sigma}^{N+1} = \sum_m U_{\mu m}^*(\mathbf{k}) \sum_{\mathbf{R}} e^{i\mathbf{k}\mathbf{R}} \Psi_{\mathbf{R}m\sigma}^{N+1}, \quad (8)$$

where  $U_{\nu n}(\mathbf{k})$  and  $U_{\mu m}(\mathbf{k})$  are the band-mixing matrices of the two Wannier transformations. The *correlated* ionization potential and electron affinity matrices  $\text{IP}_{mn'}$  and  $\text{EA}_{mm'}$  are defined in perfect analogy to Eqs. (5) and (6).

The transformed many-body wave functions  $\Psi_{\mathbf{R}n\sigma}^{N-1}$  and  $\Psi_{\mathbf{R}m\sigma}^{N+1}$  are sometimes referred to as ‘correlated local holes’ and ‘correlated local electrons’. Yet, like the Wannier functions or any other kind of localized orbitals they are pure mathematical constructions only meant to provide a convenient *local* representation of the delocalized eigenstates  $\Psi_{k\nu\sigma}^{N-1}$  and  $\Psi_{k\mu\sigma}^{N+1}$  one is looking for.

The benefit of this local representation is twofold. Firstly, the off-diagonal (or ‘hopping’) matrix elements of  $\text{IP}_{mn'}(\mathbf{R})$  and  $\text{EA}_{mm'}(\mathbf{R})$  decay rapidly with increasing distance  $\mathbf{R}$  when well-localized Wannier orbitals are used such that the (in fact infinite) summation over  $\mathbf{R}$  in Eqs. (5) and (6) can be truncated at some distance  $R_{\text{cut}}$ . Secondly, the individual local matrix elements  $\text{IP}_{mn'}(\mathbf{R})$  and  $\text{EA}_{mm'}(\mathbf{R})$  can be evaluated in *finite* clusters of the periodic system, because excitations from the involved local spin orbitals into some distant spin orbitals become negligible once they are sufficiently apart. In addition, as outlined in [2,3], asymptotic corrections can be applied to account for the missing contributions, if necessary.

To obtain the local matrix elements (LMEs) from the clusters our local Hamiltonian approach is applied to the finite cluster as well leading to a set of localized occupied and virtual orbitals  $\varphi_a$  and  $\varphi_r$  and the corresponding molecular ionization potential and electron affinity matrices  $\text{IP}_{aa'}$  and  $\text{EA}_{rr'}$ . However, instead of determining the LMEs in order to find the band energies as done for the periodic system, one now proceeds in the opposite direction. Starting from the excited-state energies  $E_v^+$  and  $E_\mu^-$  of the cationic and anionic cluster, which can be calculated (together with the molecular ground-state energy  $E_0$ ) by means of any suitable quantum chemical correlation method, the unknown LMEs are evaluated according to

$$\text{IP}_{aa'} = \sum_v E_v^+ U_{va} U_{va'}^* - E_0 \delta_{aa'} \quad \text{and} \quad (9)$$

$$\text{EA}_{rr'} = E_0 \delta_{rr'} - \sum_\mu E_\mu^- U_{\mu r}^* U_{\mu r'}. \quad (10)$$

The unitary matrices  $U_{va}$  and  $U_{\mu r}$  stem from some suitable localization such as the Foster–Boys procedure [13] (see Fig. 1) and are the molecular counter parts of the band-mixing matrices. We used the

MRCI(SD) option [14–16] of the MOLPRO program package [17] taking the unrelaxed Hartree–Fock orbitals of the neutral system to expand the wave functions of the charged molecules as well. The lack of size-consistency (SC) inherent to truncated CI schemes could be overcome by developing a special SC correction for the  $(N \pm 1)$ -electron systems [11] similar to the well-established Pople correction [18] for closed-shell systems. To facilitate the still quite demanding cluster calculations the incremental scheme was employed (see [1–3,11] for details).

Despite the formal hole-particle dualism in the equations above, there is quite a difference between valence and conduction band calculations for ab initio Hamiltonians. Virtual orbitals are much harder to localize than occupied ones, and (especially for large band gap systems) the anionic clusters tend to become electronically unstable such that special embedding techniques [19] have to be applied to make the calculations feasible. Yet, in our test system, a conjugated polymer, the energetically low-lying conduction states turn out to be sufficiently localized on the polymer to be modelled in an isolated polymer chain (for details see below).

### 3. Results

As test system for our method we chose a *trans*-polyacetylene single chain, an infinite, flat hydro-carbon molecule with alternating C–C bond lengths and  $\text{C}_2\text{H}_2$  as repeat unit (see Fig. 1). The experimental geometry of the carbon skeleton [20],  $d(\text{C–C}) = 1.45 \text{ \AA}$  and  $d(\text{C=C}) = 1.36 \text{ \AA}$  with a lattice constant of  $2.455 \text{ \AA}$ , is adopted resulting in a bond angle  $\angle(\text{C–C}, \text{C=C})$  of  $121.74^\circ$ , and the C–H bond length is  $1.087 \text{ \AA}$  (taken from [21]). Flexible correlation-consistent valence triple zeta (VTZ) basis sets [22] were used throughout, to allow reasonable correlation calculations also for the anionic  $(N + 1)$ -electron states.

X-ray scattering tells [23] that crystalline *trans*-polyacetylene (tPA) consists of weakly coupled fishbone-like packed tPA single chains all aligned in the same direction, as is also evident from the high anisotropy of the electronic properties of bulk tPA. Our HF calculation with CRYSTAL [12] gives valence band widths of 5–10 eV for crystal momenta  $\mathbf{k}$  parallel to the chains but not more than 0.4 eV in the perpendicular directions, telling that the valence orbitals of bulk tPA are well-localized on the single chains without showing any significant inter-chain coupling. The same we found for the low-lying conduction bands up to about 3 eV above the bottom of the lowest conduction band. Up to this energy the band structure of single tPA chains practically coincides with those of bulk tPA (for  $\mathbf{k}$  along to the chains). Obviously, the adopted

standard way of discretizing the continuum of the single chain by employing a finite basis set is well-suited to describe the  $\pi^*$  conduction band which models its counterpart in bulk tPA.

The band structure of a single tPA chain as obtained by our local Hamiltonian approach is depicted in Fig. 2, where it is compared to the HF data. All five valence bands and the three lowest conduction bands of tPA are shown. Evidently, the band structure changes dramatically upon inclusion of electron correlation. The valence bands shift upwards, the conduction bands downwards, and a flattening of all bands (significantly more pronounced in the valence region) is observed leading to the desired narrowing of the band gap. Other interesting but more subtle changes are also discernible, e.g., the lifting of accidental degeneracies or the narrowing of avoided crossings. The band gap of tPA reduces by 2.31 eV, from 6.42 eV on the HF level down to 4.11 eV when correlation is included. This reduction is perfect in line with similar values, 2.35 and 2.38 eV, reported in two independent studies on tPA single chains [5,6], where the  $\pi$  bands alone were investigated by means of Møller–Plesset perturbation theory (MP2). The lowest ionization potential becomes 4.58 eV, the highest electron affinity 0.47 eV, a positive value finally, indicating that *trans*-polyacetylene is able to retain an extra electron as is known from experiment [24].

The accuracy of our approach is governed by the error in the determination of the LMEs by the incremental scheme. For tPA it mainly arises from the truncation of the incremental series after the second order corrections. The discarded long range polarization effects turned out to be negligible. The resulting uncertainty in the band structure could be estimated to not exceed 0.3 eV for any  $k$ -point which is less than 1% of the total band energy range. A more detailed error analysis can be found elsewhere [11]. The new size-con-

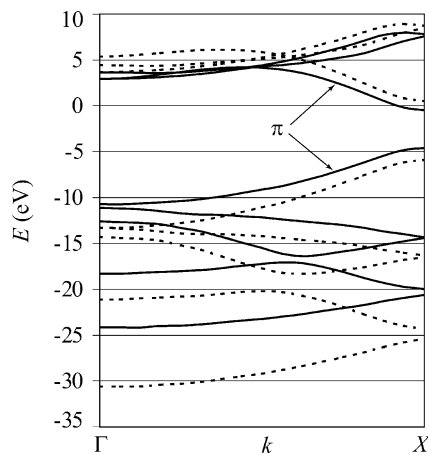


Fig. 2. Correlated (solid line) and Hartree–Fock (dashed line) band structure of an infinite *trans*-polyacetylene single chain.

sistency (SC) correction for the excited states is crucial here to reduce the SC error in the LME increments to 0.01% of the contributing correlation energies. The truncation error of the lattice summations in Eqs. (5) and (6) was analyzed on the HF level. Keeping only LMEs above 1 mHartree (which results in 59 LMEs for the valence and 39 for the conduction bands) the band energies from a canonical HF calculation with CRYSTAL could be reproduced within 0.2 eV. To account for these deviations they are added, individually for each  $k$ -point and band index, to the band energies emerging from the LMEs.

#### 4. Discussion and conclusions

In optical studies on bulk *trans*-polyacetylene [23,25,26] an absorption maximum at about 2 eV is observed. Taking into account the evidence, both experimentally and theoretically for the existence of an excitonic gap state [5,27–29], 0.4 eV below the conduction band [28], the fundamental band gap of tPA becomes 2.4 eV, which is noticeably smaller than the value of 4.1 eV we (and others [5,6]) found.  $\pi$ -band splitting due to inter-chain coupling was made responsible for that discrepancy [6], but for the experimentally found fishbone-like stacking of bulk tPA we only find a reduction of the fundamental band gap of 0.6 eV on the HF level and suppose (based on the MP2 data in [6]) a further 0.2 eV reduction upon inclusion of correlation leading to a gap of 3.3 eV. The more pronounced reductions ( $\sim 1.4$  eV) reported in [6] for two tPA chains are considered to be an artifact of the vertical tPA packing assumed there.

The missing long-range *inter*-chain polarization existing in the bulk material could be the reason why wave-function-based methods applied to tPA single chains (or stacks of a few of them) consistently overestimate the fundamental band gap of tPA, but it could also be that effects beyond bare electron correlation have to be included to achieve accordance with experiment.

Nevertheless, this study demonstrates that our local Hamiltonian approach provides a sought scheme to perform reliable wave-function-based correlation calculations for excited electron hole and attached electron states in solids and polymers with any suitable quantum chemical correlation method available, as corroborated by similar studies in our group on diamond and hydrogen fluoride chains.

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