Chapter 9

Excitation energies of oligomers

In this chapter we study the $\pi\rightarrow\pi'$ singlet excitations of the $\pi$-conjugated oligomers of polyacetylene, polydiacetylene, polybutatriene, polythiophene, poly(para-phenylene vinylene) and the lowest singlet excitations of the hydrogen chain. By studying the dependence of the excitation spectrum on the chain length we conclude that the reduction of the static polarizability when using the VK-functional has two origins. First, the excitation energies of transitions with a large transition dipole are shifted upward. Second, the HOMO-LUMO character and oscillator strength of the lowest transition within the adiabatic local density approximation is transferred to higher transitions. The lowest transitions that have a considerable oscillator strength obtained with the VK-functional have excitation energies that are in most cases in better agreement with available reference data than the adiabatic local density approximation.

9.1 Introduction

In Chapter 6 we showed that we can use time-dependent current-density-functional theory (TDCDFT) in order to go towards the solution of this longstanding problem of the overestimation of the static polarizability of long molecular chains. With this method we describe ultranonlocal exchange-correlation effects using a functional that is dependent on the current density. Vignale and Kohn proposed such a functional \cite{8,9} in which the current-density is used as a local indicator of global changes. From a careful analysis of the weakly inhomogeneous perturbed electron gas they arrived at an expression \cite{8,9,23,24} for the first-order induced exchange-correlation contributions in the form of a viscoelastic stress field. Within the VK-functional we use a parameterization of the viscoelastic coefficient based on results of Conti et al. \cite{65} for the transverse response of the homogeneous electron gas \cite{77}. For the prototype polyacetylene and many other linear conjugated oligomers the results obtained using this VK-functional significantly improved upon the ALDA results, and were in excellent agreement with high level \textit{ab initio} quantum chemical methods. However, we also observed that a similar large correction was not obtained for a hydrogen chain with alternating bond lengths,
which is seen as a theoretical model for conjugated systems (see Ref. [88] and references therein). This indicates that the VK-functional in the parameterization we use is not able to describe all features necessary for a correct treatment of the axial polarizability.

In Chapter 8 we calculated the excitation energies of a benchmark set of molecules. We studied several types of transitions. In most cases, the excitation energies of the $\pi \rightarrow \pi^*$ transitions obtained with the VK-functional were found to improve much upon the ALDA values, giving results close to other values available from literature. We also found that the $n \rightarrow \pi^*$ energies were strongly overestimated with VK and that for some other types of excitations the picture that emerges was less clear. In the $\pi$-conjugated systems studied here the low-lying $\pi \rightarrow \pi^*$ transitions determine for a large part the axial polarizability. We therefore expect that the reduction in the polarizability for these systems is linked to a modification of the $\pi \rightarrow \pi^*$ excitations.

In this chapter we study the lowest dipole-allowed singlet excitations of the oligomers of polyacetylene, polydiacetylene, polybutatriene, polythiophene, poly(para-phenylene vinylene), and the hydrogen chain. The singlet excitations considered here are all of the $\pi \rightarrow \pi^*$ type except for the hydrogen chain. We compare our results with available experimental and ab initio data. From the results for the $\pi \rightarrow \pi^*$ excitations of the small molecules and the excellent VK results for the polarizabilities of $\pi$-conjugated oligomers, we may expect a large improvement with VK upon the calculated ALDA excitation spectra.

9.2 Computational Details

All calculations were performed with our modified version of ADF [25,99-103].

For the oligomers of polyacetylene (PA), polydiacetylene (PDA), polybutatriene (PBT), polythiophene (PT) and the hydrogen chain we use the same geometry as we used in Chapter 6. This is the first chapter in which we study the poly(para-phenylene vinylene) (PPV) and polyacene (PAC) oligomers. We did a geometry optimization for these oligomers with a generalized gradient approximated potential (GGA) by Becke [35] for exchange and Perdew [148] for correlation (BP functional). We forced the oligomer geometries to be planar (C, symmetry).

All calculations were done within the standard ADF TZ2P basis set, which is a triple-zeta Slater type basis set augmented with two polarization functions. Cores were kept frozen for carbon up to 1s and for sulfur up to 2p.
In all excitation energy calculations the ground state has been calculated with the LDA functional in the VWN parameterization [34]. The response calculations themselves were done with the adiabatic local density approximation (ALDA) derived from the ground-state LDA expression and the VK-functional. For the latter we use for the singlet transitions a parameterization of the viscoelastic coefficient based on results of Conti et al. [65] for the transverse response of the homogeneous electron gas [77]. For the triplet excitation energies we use the parameterization of Qian and Vignale [60]. From now on we denote these calculations simply as ALDA and VK instead of LDA/ALDA and LDA/VK.

9.3 Results

In Sections 9.3.1 till 9.3.7 we show our results for the excitation energies of several molecular chains. In Section 9.3.2 we discuss our results for the triplet excitation energies of polyacetylene.
We discuss the prototype polyacetylene (PA) chain. In Ref. [77] we obtained axial polarizabilities for the PA oligomers that were very close to the available MP2 results if we use the VK-functional, but that were considerably overestimated when using the ALDA functional. In Figure 9-1 we plot the ALDA and VK results for the (dipole allowed) $^1B_u$ excitation energies and corresponding oscillator strengths against the number of oligomer (C$_2$H$_2$) units. We compare our data with experimental results [193] and CCSD-EOM results [192]. The $^1B_u$ excitation energies obtained within the ALDA are close to the CCSD results for the small chain lengths (3-4 units), but for the longer chains the excitation energies are underestimated. The underestimation for the longest chain of 15 units is 1.39 eV. This result is consistent with the fact that the ALDA overestimates the polarizability as can be seen from the sum-over-states (SOS) expression for the polarizability.

Figure 9-1. ALDA and VK singlet excitation energies and oscillator strengths of polyacetylene oligomers compared with CCSD-EOM [192] and experimental results. Exp. 1 and Exp. 2 are both absorption spectra from Ref. [193].

Figure 9-2. ALDA and VK HOMO-LUMO character and transition dipole moments for polyacetylene oligomers.

9.3.1 Polyacetylene
where \( \omega_n \) are the excitation energies and \( f_n \) the oscillator strengths. The reduction of the static polarizability by using the VK-functional has to be a result of a decrease of the oscillator strength of the lowest transitions or an increase of their excitation energies, or both. We therefore expect that the excitation energies calculated with VK will improve upon the ALDA. Indeed the VK results for the 1 \( ^1B_u \) excitation energy are higher than the ALDA results and lie closer to the CCSD results, but from 10 units onward they also underestimate the CCSD results.

If we look at the oscillator strengths we see that the ALDA oscillator strength of the 1 \( ^1B_u \) transition rises, although less steeply for larger chain lengths. This contributes to the large overestimation of the polarizability in case of the ALDA. The VK oscillator strength for the 1 \( ^1B_u \) transition also rises in the beginning but drops again after 5 units. The 2 \( ^1B_u \) transition has almost zero oscillator strength for all chain lengths, and for this excitation the effect of VK on the excitation energies is almost zero with values lying very close to the ALDA values. We have therefore not added this excitation to the graph. The oscillator strength of the 3 \( ^1B_u \) transition with VK rises at the point where the 1 \( ^1B_u \) oscillator strength drops. The 3 \( ^1B_u \) oscillator strength drops from 10 units onward, but then the 7 \( ^1B_u \) transition takes over. The 4 \( ^1B_u \), 5 \( ^1B_u \) and 6 \( ^1B_u \) transitions have again an oscillator strength close to zero and the VK excitation energies are close to their corresponding ALDA values. In Figure 9-2 we show the HOMO-LUMO character and the transition dipole moment in the axial direction of the \( ^1B_u \) transition. The transition dipole moment, which is mainly in the axial direction, follows the same trend as the oscillator strengths. If we look at the HOMO-LUMO character we find that the 1 \( ^1B_u \) transition has almost 100% HOMO-LUMO within the ALDA. The character of the 1 \( ^1B_u \) transition with VK is also close to 100% HOMO-LUMO for the small chains, but when the chains become longer more states mix in. Just like in case of the oscillator strength it are the 3 \( ^1B_u \) and later the 7 \( ^1B_u \) transitions that gain HOMO-LUMO character. We see that the excitations with a large spectral weight are not the lowest transitions with VK and they move to higher energy as the chain becomes longer. These transitions with the largest spectral weight lie close to the CCSD results. This is consistent with the fact that we find much lower polarizabilities for PA with VK.
9.3.2 Triplet excitation energies of polyacetylene

For polyacetylene we also calculated the triplet $^3\text{B}_u$ excitation energies. We show our results in Figure 9-3. Since the triplet excitation energies have no oscillator strength we plot the % HOMO-LUMO character instead. We have also added the difference between the Kohn-Sham HOMO and LUMO orbital energies.

From the graph we see that the ALDA values lie close to the experimental [195,196] and CIS [194] results. They also lie very close the Kohn-Sham HOMO-LUMO gap. The VK-functional has a large effect, just like in the singlet case. But in this case the effect of VK is unwanted since the ALDA values are already close to experimental and CIS values. Apart from the fact that the excitation energies lie much higher than the ALDA values, the HOMO-LUMO character is transferred to the $3^3\text{B}_u$ and later the $7^3\text{B}_u$ transitions.

The reason of this large effect of VK is that the static values of $B^1$, presented in Table 5-1, are very close to the values of $f_{\text{ex}}(0)$. Therefore we can expect a similar effect of VK for both the singlet and triplet excitation energies. Since there is not much qualitative difference between the singlet and triplet energies and there is hardly any reference data available for the triplet energies, we will not give the triplet energies for the other systems.

9.3.3 Polydiacetylene and polybutatriene

In Ref. [78] we made a comparison for the polarizabilities of the oligomers of polydiacetylene (PDA) and polybutatriene (PBT). We found that the polarizabilities obtained with VK of these two systems are very similar. The value per oligomer unit, which can be estimated from the experimental values for the polydiacetylene-like PTS (R=R’=CH$_2$OSO$_2$C$_6$H$_4$CH$_3$) and polybutatriene-like TDCU (R=R’=(CH$_2$)$_4$OCONHCH$_4$H$_3$), are also found to be close together.
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[107]. The Hartree-Fock polarizabilities for these systems were very different, the PDA result lying close to our VK values but the PBT value being much larger for the larger chains. Some CASSCF and CASPT2 results for the 1 1A’ excitation energies of PDA and the 1 1B_u excitation energies of PDA were available from the literature for the shorter chains [197]. The CASPT2 values are considered the most accurate according to Ref. [197]. There are also CCSD results available for the monomers [117]. We show these results together with our VK and ALDA results in Figure 9-4 and Figure 9-5. The oligomer unit is for both molecules a C_8H_2 unit. The trends observed for the ALDA and VK excitation energies, oscillator strengths, HOMO-LUMO character and axial transition dipole moments are again similar to the previous examples. In case of PDA the CASPT2 and CASSCF results for the excitation energies lie close to the VK values with the largest oscillator strength. For PBT CASSCF results lie close to the VK results with the largest oscillator strength, but here the CASPT2 results lie closer to the ALDA. The literature data for PBT are widely spread for the longer chain lengths, and we cannot make any conclusions on whether the VK results improve upon the ALDA. As can be seen from Figure 9-5 the oscillator strength for the 3 1B_u transition of butatriene (1 unit of PBT) with VK is larger than the oscillator strength of the 1 1B_u transition, but it turns out that the stronger 3 1B_u excitation does not correspond to a HOMO-LUMO excitation with VK. The major contribution to this transition is from the HOMO-1→LUMO+1. Therefore the 3 1B_u transition of VK should be compared with the 3 1B_u transition of the ALDA (7.58 eV for the excitation energy and 1.21 a.u. for the oscillator strength).
9.3.4 Polythiophene

In Figure 9-6 we show the excitation energies and oscillator strengths for the 1 $^1B_u$ (even number of thiophene rings) and 1 $^1B_2$ (odd number of thiophene rings) transitions of polythiophene (PT) against the number of SC$_4$H$_2$ units. The ALDA and VK results show the same behavior as observed for PA. The oscillator strength of the 1 $^1B_u$/B$_2$ transition of VK drops for longer chain lengths and the spectral weight is transferred to the 3 $^1B_u$/B$_2$ and 4 $^1B_u$/B$_2$ transitions. The 2 $^1B_u$/B$_2$ in between again has almost zero oscillator strength and the VK excitation energies lie close to the ALDA values. For the axial transition dipole moment and the HOMO-LUMO character we see the same trends as for polyacetylene, specifically the axial transition dipole moment shows the same trend as the oscillator strength and with VK the HOMO-LUMO character is transferred from the 1 $^1B_u$/B$_2$ to the 3 $^1B_u$/B$_2$ and later to the 4 $^1B_u$/B$_2$ transition. If we compare our results with the available CIS [198] and experimental [199-201] results it is clear that the ALDA underestimates the excitation energies for the long chain
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9.3.5 Poly(para-phenylene vinylene)

In Figure 9-7 we show the results for poly(para-phenylene vinylene) (PPV). We choose the trans-stilbene molecule to be zero PPV units, a new unit is obtained by adding a styrene unit between the trans-stilbene. It is immediately clear from the figures that with VK many states mix in. We see again the same trends as for the other systems studied. The ALDA values for the excitation energies strongly underestimate the experimental [203] and RCIS [202] results, especially for the longer chain lengths. The excitation energies with VK for the transitions with the largest oscillator strengths are all in between the experimental and RCIS results, the longer chains being closer to the experimental values.
9.3.6 Polyacene

In Figure 9-8 we show our results for the \(^1\text{B}_2\text{u}\) transition of polyacene (PAC) and in Figure 9-9 we show our results for the \(^1\text{B}_3\text{u}\) transition. One phenyl ring is chosen to be one unit (so naphthalene is two units). The \(^1\text{B}_2\text{u}\) transition is largely a HOMO→LUMO transition and is known as the \(L_a\) state. The \(^1\text{B}_3\text{u}\) transition is known as the \(L_b\) state and is of shared HOMO-1→LUMO and HOMO→LUMO+1 character. For both transition experimental data is available up to 8 rings [156] and we also compare with available CC2 data [156]. For the \(^3\text{B}_3\text{u}\) transition we only show the values for 3 and more rings. This is because the \(^3\text{B}_3\text{u}\) transition of naphthalene has relatively high oscillator strength, but this transition is not of the \(L_a\) type. Including it would only make the graph unclear. For the \(L_a\) state we see that the ALDA again underestimates the literature values. The VK values for the \(^1\text{B}_3\text{u}\) lie close to the literature values for the smaller chains, but for the larger chains they start to overestimate and the \(^3\text{B}_3\text{u}\) state starts to mix in. For the \(L_b\) state we see that the ALDA and VK values lie very close together and are close to the experimental values.
From the graphs we see that VK has a much larger effect on the \( L_a \) state than on the \( L_b \) state. This can be explained by looking at the transition dipole moment. The HOMO\( \rightarrow \)LUMO transition of the \( L_a \) state has a large transition dipole moment along the short axis of the molecule (not along the chain direction). The HOMO\(-1\)\( \rightarrow \)LUMO and HOMO\( \rightarrow \)LUMO\(+1\) have large transition dipole moments along the long axis of the molecule, but these transition dipole moments counteract each other. The \( L_a \) state therefore has only a small net transition dipole moment along the chain direction. This explains the small effect of the VK-functional.

An important point that is not immediately clear from the graph is the ordering of the \( L_a \) and \( L_b \) states. For naphthalene the experiment tells us [169] that the \( L_b \) state should be below the \( L_a \) state, while for anthracene and onwards the \( L_a \) state should be below the \( L_b \) state. Within the ALDA the \( L_a \) state is always below the \( L_b \) state even for anthracene. VK corrects for this discrepancy and predicts the right ordering of the \( L_a \) and \( L_b \) states.
9.3.7 The model hydrogen chain

Finally we studied the hydrogen chain. In Ref. [77] we showed that VK only has a minor effect on the polarizability of the model hydrogen chain. In Figure 9-10 and Figure 9-11 we show our results for the $1\text{A}_2u$ transition for ALDA and VK. To our knowledge no literature results are available for this system. We see that VK has hardly any effect on the excitation energies of the hydrogen chain. For the really long chains the $3\text{A}_2u$ transition takes over from the $1\text{A}_2u$ transition for VK but the effect is small. If we look at the HOMO-LUMO character we see that even for the long chains the HOMO-LUMO character is still >90% with VK.

9.4 Discussion

For all systems studied here we see the same trends. With VK the oscillator strength, axial transition dipole moment and HOMO-LUMO character are transferred to higher states. In all cases the excitation energies obtained with VK lie higher than the ALDA values. Except for the model hydrogen chain and PBT the excitation energies obtained with VK that have the largest
excitations along axial the 3 transition ALDA. ALDA observe strength 7 when the transition. oscillator strengths of polyacetylene.

transition within the ALDA. Here all transition the B 1u 1 transition. For example, see ALDA 9-12. B 1u 1 transition within the same oscillator strengths through ALDA and VK. For example, see ALDA 5-7 B 1u 1 transition within the ALDA and VK. We also see in Figure 9-12 that the ALDA gains oscillator strength for the long chains. With VK this excitation gets mixed in with several higher states and it is difficult to see which VK state corresponds with the transition. We observe the same phenomenon when the 3 B 1 transition “pushes through” the 4 B 1 transition. We saw in Ref. [79,80] that in case of π→π’ transitions a large oscillator strength (and a large transition dipole moment) means a large VK effect. This is exactly what we observe here. The excitation energies with little oscillator strength do not shift compared to the ALDA and the transitions with a large oscillator strength have a large shift compared to the ALDA. We see the same for the other systems studied. We also see in Figure 9-12 that the ALDA moves away from the 1 B 1 transition of the ALDA until it comes to the 2 B 1 transition. We see that at this point the 3 B 1 transition starts to move away from the ALDA, as if the 1 B 1 transition “pushes through” the 2 B 1 transition. We observe the same phenomenon when the 3 B 1 transition “pushes through” the 4 B 1, 5 B 1, and 6 B 1 transitions and becomes the 7 B 1 transition. We saw in Ref. [79,80] that in case of π→π’ transitions a large oscillator strength (and a large transition dipole moment) means a large VK effect. This is exactly what we observe here. The excitation energies with little oscillator strength do not shift compared to the ALDA and the transitions with a large oscillator strength have a large shift compared to the ALDA. We see the same for the other systems studied. We also see in Figure 9-12 that the 1 B 1 transition within the ALDA gains oscillator strength for the long chains. With VK this excitation gets mixed in with several higher states and it is difficult to see which VK state corresponds with the 3 B 1 transition within the ALDA.

In all systems studied here the excitations with large oscillator strengths also have a large axial transition dipole moment. This means that there is a large global displacement of charge along the long axis of the molecule, which means a large current flow and a large VK effect. The excitations for which the oscillator strengths and transition dipole moments are small have only spectral weight are closer to the available literature results. This explains why we obtain lower values for the polarizability with VK. However the individual excitation energies and oscillator strengths are not correctly described with VK.

In Figure 9-12 we again show the excitation energies and oscillator strengths of PA, but this time we added all transitions up to 4 B 1 for both ALDA and VK (to keep the graph readable we do not show the higher transitions). The ALDA and VK energies for the 2 B 1 and 4 B 1 transitions lie very close together. As mentioned the oscillator strengths for these transitions are very small. The 1 B 1 transition of VK moves away from the 1 B 1 transition of the ALDA until it comes close to the 2 B 1 transition. We see that at this point the 3 B 1 transition starts to move away from the ALDA, as if the 1 B 1 transition “pushes through” the 2 B 1 transition. We observe the same phenomenon when the 3 B 1 transition “pushes through” the 4 B 1, 5 B 1, and 6 B 1 transitions and becomes the 7 B 1 transition. We saw in Ref. [79,80] that in case of π→π’ transitions a large oscillator strength (and a large transition dipole moment) means a large VK effect. This is exactly what we observe here. The excitation energies with little oscillator strength do not shift compared to the ALDA and the transitions with a large oscillator strength have a large shift compared to the ALDA. We see the same for the other systems studied. We also see in Figure 9-12 that the 1 B 1 transition within the ALDA gains oscillator strength for the long chains. With VK this excitation gets mixed in with several higher states and it is difficult to see which VK state corresponds with the 3 B 1 transition within the ALDA.

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a small global charge displacement (small current) and therefore the VK effect is small. The problem with VK seems to be that the transitions with small oscillator strengths do not shift upward like the transitions that do have large oscillator strengths. When transitions with large and small oscillator strength become close in energy, they can mix and the oscillator strength becomes distributed over these states. The mean weighted average of the excitation energies is however roughly at the correct position.

Finally we looked at the triplet 'B_u transition in polyacetylene. We saw again a large effect of VK and HOMO-LUMO character being transferred to higher transitions. But in this case the effect of VK is unwanted, the ALDA values are already close to experimental and CIS values. The reason of this large effect of VK is that the static values of B', presented in Table 5-1, are very close to the values of $f_{\text{exc}}(0)$. Therefore we can expect a similar effect of VK for both the singlet and triplet excitation energies. This is indeed what we find.

9.5 Conclusion

We calculated the excitation spectra for several $\pi$-conjugated oligomers with the VK-functional. For these systems we found in our previous studies [77,78] that the axial polarizability obtained with VK lies close to the literature values, while the ALDA strongly overestimates. Previously we also studied the $\pi \rightarrow \pi'$ transitions of some small $\pi$-conjugated systems and found an improvement of the excitation energy when using VK. In this work we find that the excitation energies, underestimated within the ALDA, are always increased by VK. For the triplet case we saw that the VK overestimates the excitation energies. For the singlet case we find that VK transfers the oscillator strength to higher excitations but that the transitions with small oscillator strengths do not shift upward like the transitions that do have large oscillator strengths. This leads to the fact that individual excitation energies and oscillator strengths are not correctly described with VK. We did observe that the VK singlet transitions that have the largest spectral weight lie close to the available literature results for all systems except PBT and the hydrogen chain.