Time-dependent density functional theory for periodic systems
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Infinite conjugated polymeric chains

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9.1 Abstract

The linear optical polarizability of several infinite conjugated polymers is examined within the time-dependent density functional theory approach, by making use of the periodicity in these systems. The polymeric chains studied were the model system polyhydrogen (H), polyacetylene (PA), polydiacetylene (PDA), polybutatriene (PBT), polythiophene (PT), polysilane (PSi) and polymethineimine (PMI). The results for the longitudinal polarizability, i.e., along the polymeric backbone $\alpha_{zz}$, were highly overestimated by TDDFT in comparison with the more traditional calculation methods (like e.g., Hartree-Fock and coupled cluster) for all the considered polymeric chains. The overestimation is most likely due to the incorrect description of the macroscopic exchange-correlation (xc) electric field contribution by the LDA and GGA approximation for the xc-functional. An estimate for this macroscopic exchange-correlation contribution $E_{xc,mac}$, is given for the polymeric chains considered.

9.2 Introduction

There is currently a lot of interest in the linear and nonlinear optical (NLO) properties of large polymeric systems due to the application of these systems in optical and photonic devices. The polarizability component along the backbone of the polymeric chains, and in general also the big NLO response, increases with the chain length and with the degree of $\pi$-conjugation, which are well known phenomena caused by the electron delocalization along the backbone in these polymeric chains. The calculations of several properties of these $\pi$-conjugated chains, requires the inclusion of electron correlation effects to achieve accurate results. The correlation effects are known to be large in these systems with multiple and single bonds. Over the years many techniques have been developed, which are able to deal successfully with the electron correlation effects like, Möller-Plesset (MP),
configuration interaction (CI), coupled cluster (CC) and multiconfiguration self-consistent field (MCSCF). These approaches become too time consuming when considering the more interesting (longer) systems in material science, because of their high and unfavourable computational needs. Another method, which scales much more favourable in computational costs than the more conventional methods is density functional theory (DFT), which, in principle, also handles the electron correlation effects correctly. Therefore the methods based on DFT have gained much in popularity in \textit{ab initio} quantum chemistry over the last years [13, 14]. As mentioned before, the NLO properties are currently under intense study, and, when using DFT, calculations are now feasible on the more interesting longer conjugated polymeric systems as well. In such systems the polarizability grows non-linearly with increasing chain length. The polarizability per unit cell, increases rapidly for the shortest chain lengths, then saturates and becomes near-constant for the longest chains.

For the determination of the asymptotic polarizability per unit cell, two different approaches can be followed. In the first one, one repeats the calculations to determine the characteristics and properties of the polymeric systems of varying length. The calculated polymers thereby consist of an increasing number of the same monomeric units. The infinite polymeric chain limit is obtained by extrapolating these results. This approach has the disadvantage that the onset of the saturation can be slow in the more conjugated and more interesting systems, and that the asymptotic values for the polarizability are often highly sensitive to the extrapolation model, which is always needed in this approach (See Section 9.4).

The alternative approach is to apply the methods of polymer quantum chemistry which make use of the periodicity in these polymeric systems, and perform a band structure calculation. In recent years only uncoupled and coupled Hartree-Fock (UHF/CHF) methods have been developed to calculate the polarizabilities per unit cell of the infinite polymeric chains.

In this chapter we apply the second approach and investigate the suitability of the first approach for determining the polarizability of several $\pi$-conjugated systems by employing conventional DFT schemes, while using different exchange-correlation functionals. The pioneering work in this area by others [160, 161], resulted in a number of conclusions considering DFT; (i) the correlation correction obtained in such systems is either much too small or even in the wrong direction, causing $\alpha$ to be overestimated; (ii) the chain length dependence is excessively large, in particular for the more alternating systems. These failures by DFT were attributed to the short-sighteness of the xc potentials, causing them to be insensitive to the polarization charge at the ends of the polymeric chain. After some further analysing [162], the failure was traced back to originate from an incorrect electric field dependence of the ‘response part’ of the xc potential in both the local, and the gradient corrected density approximations. The xc-approximations do not correctly predict a linear term counteracting the applied electric field.

We compare in this chapter the above (overestimated) DFT results (first approach) for the asymptotic longitudinal polarizability of the $\pi$-conjugated polymeric chains with the ones as obtained directly by our recently implemented periodic band structure TDDFT approach (second approach) [63, 94].
9.3 DFT versus other calculation methods

Nowadays several methods exist for calculating the polarizabilities of molecular systems. Some of these methods include correlation effects, others do not. In general, when a centrosymmetric molecule is placed in a static homogeneous electric field $F_0$, the energy $E$ of the molecule is stabilized according to

$$E = E_0 - \frac{1}{2!} \alpha_{ij} F_0^i F_0^j - \frac{1}{4!} \gamma_{ijkl} F_0^i F_0^j F_0^k F_0^l - \ldots ,$$

(9.1)

in which the summation over repeated indices is implied, $\alpha$ and $\gamma$ are the polarizability, and second hyperpolarizability tensors, and $E_0$ is the energy of the free molecule. The $i$-th component of the dipole moment of the molecule, which is induced by this electric field, is given by

$$\mu_i = \alpha_{ij} F_0^j + \frac{1}{3!} \gamma_{ijkl} F_0^i F_0^j F_0^k F_0^l + \ldots .$$

(9.2)

Among the available calculation methods the molecular polarizability is obtained in different ways. The polarizability is defined, either as the linear response of the dipole moment to an external electric field, or as the second-order derivative in the perturbation expansion of the electronic energy with respect to the electric field. These definitions are equivalent due to the Hellmann-Feymann theorem, and we can write

$$\alpha = - \left( \frac{\partial^2 E}{\partial F^2} \right)_{F=F_0} = \left( \frac{\partial \mu}{\partial F} \right)_{F=F_0} .$$

(9.3)

Therefore, by using these techniques one needs to know the wave functions and energies of the system in the presence of the perturbation by the electric field, or equivalently, the derivatives of the wave functions and energies with respect to this electric field. These methods, which take the field-induced electron reorganization effects into account in a self consistent way, are said to be coupled methods. Examples are the coupled Hartree-Fock (CHF), the Møller-Plesset (MP), and the Configuration Cluster (CC) methods. In other uncoupled methods, which do not include field-induced electron reorganization effects, like e.g. uncoupled Hartree-Fock (UCHF), the polarizability tensor is obtained by a summation over states (SOS) procedure:

$$\alpha = 2 \sum_{n \neq 0} \frac{|\langle \psi_0 | r | \psi_n \rangle|^2}{E_n - E_0} ,$$

(9.4)

in which the sum runs over all the excited states of the system. Here $\psi_0$ and $\psi_n$ are the ground- and the excited state wave functions with corresponding energies $E_0$ and $E_n$, respectively.

In Density Functional Theory (DFT), the electron density $\rho(r)$ is the central quantity which determines all the properties of the system [13, 14]. The density $\rho(r)$ is evaluated self-consistently by solving the Kohn-Sham equation [3] which involves the evaluation of the exchange and correlation terms. The calculated results, depend on the particular approximations for the exchange-correlation functional. Several studies have already
demonstrated how accurate and useful DFT calculations can be, e.g., for the prediction of ground state geometries, atomization energies, vibrational frequencies and the energies of reactions. The results are of comparable quality as MP2 calculations, but at much lower computational costs.

9.4 Extrapolation procedures

As was already mentioned in the introduction of this chapter, the calculations to determine the characteristics and properties of the infinite polymeric chains consisted of studying the asymptotic behaviour of oligomers increasing in length, i.e., by successive addition of the same monomer unit. The extrapolations of these results to the infinite polymeric chain limit, which is necessary to determine the asymptotic longitudinal polarizability per unit cell, are often highly sensitive to the extrapolation model used, and an extrapolation scheme always has the disadvantage that the onset of the saturation can be very slow in the more conjugated and interesting systems. For the CHF, MP4, and CCSD results, given in the Tables 9.1 and 9.2, one of the following extrapolation procedures was used.

For evaluating and finding the variation in the longitudinal polarizability between consecutive oligomers, the first (most simple and fundamental) formula is

$$\Delta \alpha_{zz}(N) = \alpha_{zz}(N)/N,$$

(9.5)

in which $N$ is the unit cell number. Comparing Eq. 9.5 with the differential approach

$$\Delta \alpha_{zz}(N) = \alpha_{zz}(N) - \alpha_{zz}(N - 1),$$

(9.6)

shows that Eq. 9.6 has the advantage that it eliminates, the chain-end effects of the oligomer in the polarizability increase.

In addition to the above two extrapolation formulas, there are several ad-hoc model functions used, for finding the asymptotic value of the polarizability\textsuperscript{[174]} of the polymer. Namely,

$$\Delta \alpha_{zz}(N) = a + \frac{b}{N} + \frac{c}{N^2},$$

(9.7)

$$\Delta \alpha_{zz}(N) = a + be^{-cN},$$

(9.8)

$$\Delta \alpha_{zz}(N) = \frac{a}{1 + be^{-cN}}.$$

(9.9)

The advantage of the function in Eq. 9.7 is, that it can be systematically improved by adding higher terms in $1/N$. The model function in Eq. 9.8 has been used to predict the polymeric $\Delta \alpha_{zz}(N)$ of polyacetylene chains (Ref.\textsuperscript{[172]}), and the last one (Eq. 9.9) is called the logistic equation.

Until now there is no reason to prefer one of the above model functions, since the correct analytic form of the equation which describes the evolution of $\Delta \alpha_{zz}(N)$ with chain length is not known. A complete discussion on extrapolation techniques can be found in the Refs.\textsuperscript{[163]} and\textsuperscript{[164]}. 

9.5 Theory

When a system is perturbed by applying a time-dependent external electric field $E_{\text{ext}}(r,t)$, the density will become time-dependent and currents will be induced, so the system will become polarized. In the time-dependent (TD) version of density functional theory (DFT), one adds time-dependent vector and scalar contributions to the effective ground state potential. These additional potentials, respectively $A_{\text{eff}}(r,t)$ and $\delta v_{\text{eff}}(r,t)$, have the property that they produce the exact time-dependent density and current of the true system, when applied to the Kohn-Sham system of non-interacting particles. According to the Runge-Gross theorem [4], the time-dependent extension of the Hohenberg-Kohn theory [2, 3], these potentials are, apart from the usual freedom of choice for the gauge, functionals of the density and the current, and should therefore be obtained self-consistently. The time-dependent Kohn-Sham system is now obtained by replacing both the ground state momentum operator by

$$p \rightarrow -i\nabla + 1/c A_{\text{eff}}(r,t),$$

and the effective scalar potential by the time-dependent version

$$v_{\text{eff}}(r) \rightarrow v_{\text{eff},0}(r) + \delta v_{\text{eff}}(r,t).$$

When one neglects the small microscopic contributions to the transverse vector potential (such as the Breit term [40]), we can make a special choice for the gauge, which we will call the microscopic Coulomb gauge [63]. In this gauge both the scalar and vector potential are lattice periodic, and have the property that all microscopic components are included in the scalar potential, whereas all macroscopic components are described by the vector potential. The perturbing potentials can be given in this gauge as,

$$A_{\text{eff}}(r,t) = A(r,t) = -c \int dt' E_{\text{mac}}(r,t'),$$

$$\delta v_{\text{eff}}(r,t) = \delta v_{\text{mic}}(r,t) + \int dr' \frac{\partial v_{\text{xc}}[\rho](r')}{\partial \rho(r')} \bigg|_{\rho_0} \delta \rho(r', t).$$

Here $\delta v_{\text{mic}}(r,t)$ is the microscopic part of the Hartree potential of the induced density $\delta \rho(r,t)$. In these relations we have neglected any macroscopic contributions of the exchange-correlation (xc) in the vector potential [108], and we used the adiabatic local density approximation (ALDA) for the first order xc-contribution to the scalar potential. The macroscopic electric field $E_{\text{mac}}(r,t)$ is the average field in a region around $r$ inside the solid, and hence it comprises both the externally applied field $E_{\text{ext}}(r,t)$ plus the macroscopic part of the induced field. This latter field is in addition to the induced charge density also due to the induced current density $\delta j(r,t)$. We will treat this macroscopic field as the perturbing field. The quantity of interest (written in the frequency domain) is the induced macroscopic polarization $P_{\text{mac}}(\omega)$, which will be proportional to the macroscopic electric field $E_{\text{mac}}(r,t)$, and also to the average induced current density $\delta j(r,\omega)$, according to,

$$P_{\text{mac}}(\omega) = \chi_e(\omega) \cdot E_{\text{mac}}(\omega) = \frac{i}{\omega V} \int_V d\mathbf{r} \delta j(\mathbf{r},\omega).$$
Within time-dependent linear response theory, we obtain the following relation for the induced density,

\[ \delta \rho(r, \omega) = \int \left( \frac{i}{\omega} \chi_{ij}(r, r', \omega) \cdot E_{mac}(\omega) + \chi_{pp}(r, r', \omega) \delta v_{eff}(r', \omega) \right) dr'. \] (9.15)

The various Kohn-Sham response functions can be obtained from the occupied \((i)\) and virtual \((a)\) states of the ground-state system. They can be evaluated using the general form,

\[ \chi_{ab}(r, r'; \omega) = \frac{V}{4\pi^3} \sum_{i,a} \int d\mathbf{k} \frac{a_{ia}(r) b_{ak}^*(r')}{\epsilon_{ik} - \epsilon_{ak} + \omega + i\eta} + c.c.(-\omega), \] (9.16)

by substituting for \(a_{ia}(r)\) and \(b_{ik}(r)\) either the transition density,

\[ \rho_{ia}(r) = \psi_{ik}^*(r) \psi_{ak}(r), \] (9.17)

or the transition current,

\[ j_{ia}(r) = \psi_{ik}^*(r) \nabla \psi_{ak}(r) - (\nabla \psi_{ik}^*(r)) \psi_{ak}(r). \] (9.18)

The Brillouin zone integrations in Eq. 9.16 are evaluated numerically, by including the energy denominator in the integration weights. The way these integration weights are obtained is subject of the Appendix (See Section 9.9).

Now, by keeping the macroscopic field fixed, and noting that within the ALDA the effective potential is a functional of the density alone, we can solve the set of response equations, Eqns. 9.13 and 9.15, self-consistently. With the perturbing effective potentials now fully determined, the induced paramagnetic current density \(\delta j_p(r, \omega)\) follows from

\[ \delta j_p(r, \omega) = \int \left( \frac{i}{\omega} \chi_{ij}(r, r', \omega) \cdot E_{mac}(\omega) + \chi_{jp}(r, r', \omega) \delta v_{eff}(r', \omega) \right) dr'. \] (9.19)

The total induced current contains, apart from this paramagnetic term, also the diamagnetic contribution,

\[ \delta j_d(r, \omega) = \frac{1}{c} \rho_0(r) A(r, \omega). \] (9.20)

In the special case in which we choose the macroscopic field along one of the Cartesian directions \(j\), and with a frequency dependence according to \(E_{mac}(\omega) = -i\omega e_j\), the diamagnetic contribution to the current density reduces to \(\delta j_d(r, \omega) = -\delta j_p(r, 0)\), i.e. to minus the static paramagnetic value [63]. The paramagnetic and diamagnetic components together form the total current, of which the average value yields the macroscopic polarization. The Cartesian components of the susceptibility follow from the Eq. 9.14,

\[ [\chi_e(\omega)]_{ij} = \left\{ \frac{-1}{V \omega^2} \int_V [\delta j_p(r, \omega) - \delta j_p(r, 0)]_i dr \right\} E_{mac}(\omega) = -i\omega e_j. \] (9.21)

Under the assumption that in linear polymeric chains there is no macroscopic screening, i.e., the induced electric field in the chains is not of macroscopic nature, the macroscopic
electric field equals the externally applied electric field \( (E_{mac} \equiv E_{ext}) \). The longitudinal polarizability, along the backbone of the polymer \( \alpha_{zz} \), can be obtained as the integrated susceptibility \( \chi_e(r, \omega) \) over the unit cell

\[
\mu = \int P(r, \omega) \, dr = \left( \int \chi_e(r, \omega) \, dr \right) \cdot E_{ext} (\omega) = \alpha \cdot E_{ext} (\omega) .
\] (9.22)

### 9.6 Basis sets and parameters in the calculations

For the time-dependent density functional theory (TDDFT) calculations, we used the Amsterdam Density Functional (ADF) program [38] for the molecular calculations, and the periodic band structure calculations were performed with the Amsterdam Density Functional BAND-structure program (ADF-BAND) [37]. The basis sets in the molecular ADF and the periodic ADF-BAND calculations were triple zeta s, p Slater-type basis functions (STO’s) plus a polarization function, which we denote as 3Z2P*. For the integration in the 1-dimensional reciprocal space we used 7 symmetry unique \( k \)-points for all oligomers. The geometries for all the polymeric chains examined are depicted in Fig. 9.4, as they were found in the Refs. [161, 167, 168, 169, 170, 171, 172, 173, 174, 176].

### 9.7 Results

#### 9.7.1 The model system polyhydrogen

The infinite molecular hydrogen chain model \((H_2)_n\) has been studied extensively by Champagne and co-workers [165, 166]. The main objectives of these studies were to determine the electron-electron interaction and the size of atomic basis set needed to correctly estimate the asymptotic static longitudinal polarizability per unit cell of a polymeric system. Their results already pointed out the importance of developing direct techniques, which are able to deal with the periodicity in such systems to get the asymptotic values for the polarizability directly.

We extended our time-dependent periodic band structure DFT approach [63], which had already proven to be very succesfull for crystals [94, 102, 136, 180], to handle also systems which possess only periodicity in one dimension. This periodic TDDFT approach is used to get the asymptotic values for the longitudinal polarizability directly for the polymeric chains without the use of an extrapolation model, as is always necessary in the molecular programs.

The periodic implementation was first used for calculations on the model system polyhydrogen. We considered chains in which the unit cell length \( (a) \) (See Fig. 9.4) was varied from 4.5 to 22.0 a.u. and the intramolecular distance \( (H-H) \) was fixed at 2.0 a.u. Resulting in a bond length alternation (BLA) from 0.5 to 18.0 a.u. (See Table. 9.1)

In Table. 9.1, the asymptotic longitudinal polarizabilities \( (\alpha_{zz}) \) per unit cell (containing one \( H_2 \)-unit) of different alternating model hydrogen chains are given. The polarizabilities were
calculated by using several different calculation methods, all with different (comparable) basis sets. The basis used in the coupled Hartree-Fock (CHF), the Möller-Plesset (MP4) and coupled cluster (CCSD(T)) calculations [165] and in the G92/DMol calculations [160] were Gaussian triple-ζ plus polarization (6)-311G(∗)∗ atomic basis sets. Basis sets, which are comparable to the STO 3Z2P* used in the TDDFT calculations by the ADF [38] and the BAND [37] program.

Table 9.1: Asymptotic longitudinal polarizabilities (α_{zz}) per H₂ unit of the model system polyhydrogen with different bond length alternation, as calculated at the CHF, MP4 and CCSD(T) level in comparison with several TDDFT (ADF/BAND/G92/DMol) calculations (all values in atomic units).

<table>
<thead>
<tr>
<th>BLA</th>
<th>CHF^a</th>
<th>MP4^a</th>
<th>CCSD(T)^a</th>
<th>ADF^b</th>
<th>BAND</th>
<th>G92/DMol^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>55.079</td>
<td>53.564</td>
<td>50.632</td>
<td>162.00</td>
<td>121.9</td>
<td>139.087</td>
</tr>
<tr>
<td>1.0</td>
<td>28.602</td>
<td>26.508</td>
<td>25.666</td>
<td>47.02</td>
<td>46.2</td>
<td>48.338</td>
</tr>
<tr>
<td>2.0</td>
<td>17.682</td>
<td>15.826</td>
<td>15.511</td>
<td>22.14</td>
<td>22.2</td>
<td>21.753</td>
</tr>
<tr>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td>12.57</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
<td>12.06</td>
<td>11.7</td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td></td>
<td></td>
<td></td>
<td>11.94</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td></td>
<td></td>
<td></td>
<td>11.92</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>∞</td>
<td></td>
<td></td>
<td></td>
<td>11.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^aRef. [165] ^bRef. [38] ^cRef. [160]

The results in Table 9.1, for the asymptotic longitudinal polarizabilities of the model system polyhydrogen with different BLA, are also depicted in Fig. 9.1.

Figure 9.1: Comparison of the asymptotic longitudinal polarizabilities α_{zz} of the model (H₂)ₙ-chains with different BLA. The TDDFT based methods in comparison with others, as given in Table 9.1 (all values in atomic units).

As can be seen from Fig 9.1, the shorter the BLA in the model hydrogen chain the higher the overestimation of the polarizability in the TDDFT based methods in comparison to the other methods. Further we see from Table 9.1 that the molecular based ADF program...
and the periodic BAND implementation gave approximately the same overestimated results, which converged in the chains with the longest BLA to the polarizability of a single H$_2$-molecule. The different extrapolation procedures used in the *molecular* programs for evaluating the asymptotic value of the longitudinal polarizability are plotted in Fig. 9.2, for the model system polyhydrogen (H$_2$)$_n$ with a BLA of 0.5 Å. This was done by repeating the polarizability calculations of successive polyhydrogen chains, by increasing the length of the chain through the addition of more monomeric H$_2$-units. The extrapolation procedures used, are given in Eqs. 9.5 and 9.6, respectively. The polarizability values $\alpha_{zz}$ are plotted against the number of H$_2$-units (Fig. 9.2).

As can be seen in Fig. 9.2, the value for the by TDDFT calculated value of the longitudinal polarizability of an infinite model (H$_2$)$_n$-chain with a BLA of 0.5 Å, as found directly by our *periodic* ADF-BAND implementation, is consistent with the extrapolated asymptotic *molecular* ADF result. The use of the periodic ADF-BAND implementation is therefore much more convenient, because 1. the polarizability value is found in a single calculation, 2. the extrapolation step, for finding $\alpha_{zz}$, is not necessary, and 3. no choice for a particular extrapolation model is needed. Looking at Fig. 9.2, it should also be concluded, that the extrapolation models as given by Eq. 9.5 and 9.6 are reasonably reliable, but that the differential approach (Eq. 9.6), which eliminates the chain-end effects in the oligomers, converges much faster.

Earlier, van Gisbergen et al.[162] attributed the overestimation of the longitudinal polarizability in the model system polyhydrogen (H$_2$)$_n$-chain to an incorrect electric field dependence of the xc-potential. The LDA potential lacks a linear term, which is counteracting the externally applied electric field. From Fig. 2 in Ref. [162] it can be deduced that, when an externally applied electric field with a strength of $10^{-3}$ a.u. ($E_{\text{ext}} = 0.001$ a.u.) is applied to a model (H$_2$)$_n$-chain with a BLA of $\sim 3$ a.u., the strength of the counteracting field of which LDA lacks has a strength of $10^{-4}$ a.u. In Chapter 7, we introduced an
approximate xc-functional for the macroscopic xc-electric field. We can now estimate the value for the \( Y \)-functional needed to correct the differences between the HF and TDDFT results. Using the expression
\[
P = \tilde{\chi} \left( E_{\text{ext}} - Y \cdot P \right),
\]
and requiring the corrected longitudinal polarizability per \( \text{H}_2 \) unit to be equal to the HF value for the model \((\text{H}_2)_n\)-chain with a BLA of \( \sim 3 \) a.u., as it was deduced from the HF results in Table 9.1. We find an \( Y \)-value of 0.01. This value of \( 10^{-2} \) for \( Y \) is also found in the periodic ADF-BAND calculations. Current density functional theory gives an explicit expression for \( Y \) (See Chapter 7), and we are currently investigating if this functional indeed reproduces this value of \( 10^{-2} \) for \( Y \).

### 9.7.2 Other polymeric chains

After using the periodic TDDFT approach to get the asymptotic values for the longitudinal polarizability for the *model* system polyhydrogen \((\text{H}_2)_n\), we also calculated the \( \alpha_{zz} \) for several *real* polymeric systems, and compared our TDDFT results to the (extrapolated) CHF results. The investigated polymeric chains were polyyne (PY, \( \text{C}_{2n}\text{H}_2 \)), polyacetylene (PA, \( \text{C}_{2n}\text{H}_{2n+2} \)), polydiacetylene (PDA, \( \text{C}_{4n}\text{H}_{2n+2} \)), polybutatriene (PBT, \( \text{C}_{4n}\text{H}_{2n+2} \)), polythiophene (PT, \( \text{C}_{8n}\text{S}_{2n}\text{H}_{4n+2} \)), polysilane (PSi, \( \text{Si}_{2n}\text{H}_{4n+2} \)), and polymethineimine (PMI, \( \text{C}_{n}\text{N}_{n}\text{H}_{n+2}, \text{trans-transoid} \)). The structures and geometries of the polymers examined are depicted in Fig. 9.4. The results for the longitudinal polarizability have been collected in Table 9.2, for the polymers examined, as calculated by CHF and by our periodic TDDFT implementation (BAND). From the ratio’s of the BAND and CHF values listed in Table 9.2, it can be seen that TDDFT in the ALDA gives longitudinal polarizability for these polymers, which are overestimated by a factor of 2 to 5 compared to the CHF results. The overestimation by TDDFT is also depicted in Fig. 9.3.

![Figure 9.3: TDDFT versus CHF results for the asymptotic longitudinal polarizability of the polymers: PY, PA, PDA, PT, PSi, and PMI.](image)

As was already discussed in Section 9.7.1 for the model system polyhydrogen \((\text{H}_2)_n\), the overestimation of \( \alpha_{zz} \) by TDDFT is due to an incorrect electric field dependence of the xc-potential, which lacks a linear term counteracting this externally applied electric field.
In the same way as was done for the \((H_2)_n\)-chains, we can calculate and give a numerical value of this linear counteracting term, which is given in Table 9.2 for the investigated polymeric chains, showing that an \(Y\)-value in the order of \(10^{-3}\) is needed. This value of \(Y\), for the real polymeric systems, is in the same order as found for the model system polyhydrogen, but again it remains to be seen if this value can be reproduced by current density functional theory.

Table 9.2: Comparison of the asymptotic longitudinal polarizabilities of polyyne (PY), polyactelene (PA), polydiacetylene (PDA), polybutatriene (PBT), polythiophene (PT), polysilane (PSi) and polymethineimine (PMI), as calculated by CHF and TDDFT (all values in atomic units).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Geometry unit cell</th>
<th>BLA (Å)</th>
<th>CHF</th>
<th>TDDFT BAND</th>
<th>Ratio BAND/CHF</th>
<th>(Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY</td>
<td>([C_{2n}])</td>
<td>0.166(^{j})</td>
<td>151±2(^{j})</td>
<td>412.2</td>
<td>2.73</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.220(^{a})</td>
<td>113.5±1.5(^{i})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>([C_{2n}H_{2n}])</td>
<td>0.112(^{b,n})</td>
<td>160.5±1.5(^{k})</td>
<td>493.9</td>
<td>3.08</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.082(^{c})</td>
<td>220.7(^{f})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDA</td>
<td>([C_{4n}H_{2n}])</td>
<td>0.225;0.088(^{e})</td>
<td>226±2(^{e})</td>
<td>1138.2</td>
<td>5.04</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.230;0.100(^{d})</td>
<td>203±4(^{l})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBT</td>
<td>([C_{4n}H_{2n}])</td>
<td>0.194;0.128(^{e})</td>
<td>1060±14(^{e})</td>
<td>2498.6</td>
<td>2.36</td>
<td>0.001</td>
</tr>
<tr>
<td>PT</td>
<td>([C_{8n}S_{2n}H_{4n}])</td>
<td>0.064(^{f})</td>
<td>380.0(^{f})</td>
<td>914.8</td>
<td>2.41</td>
<td>0.002</td>
</tr>
<tr>
<td>PSi</td>
<td>([Si_{2n}H_{4n}])</td>
<td>0.0(^{g})</td>
<td>131.4±0.2(^{m})</td>
<td>182.1</td>
<td>1.39</td>
<td>0.002</td>
</tr>
<tr>
<td>PMI</td>
<td>([C_{n}N_{n}H_{n}])</td>
<td>0.100(^{h})</td>
<td>122.6±0.9(^{h})</td>
<td>572.3</td>
<td>4.67</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Figure 9.4: Polymers. The bond lengths are given in a.u., the bond angles in deg.
9.8 Conclusions

In this chapter we investigated the longitudinal polarizability of several infinite conjugated polymers, as calculated by time-dependent density functional theory. Our TDDFT implementation makes direct use of the periodicity in these systems. The TDDFT polarizabilities for the model H₂-chains, as found by our periodic BAND implementation, were close to the molecular ADF results, found after extrapolation. Both, BAND as well as ADF, overestimated the \( \alpha_{zz} \) in the model system polyhydorgen, and the overestimation is largest for the smallest BLA. The extrapolation procedures which are used in the molecular programs for calculating the static longitudinal polarizability are reasonably reliable, but it is much more convenient to do a periodic BAND calculation, in which the extrapolation step is superfluous. The same polarizability overestimation was also found for all the polymeric chains considered. This overestimation is caused by an incorrect electric field dependence of the xc potential. The LDA and GGA potentials lack a linear term, the macroscopic exchange-correlation electric field, which counteracts the externally applied electric field. The macroscopic exchange-correlation contribution \( E_{xc,mac} \) is estimated by the value of the polarization functional \( \mathbf{Y} \). The \( \mathbf{Y} \)-value is found to be in the order of \( 10^{-2}/10^{-3} \) a.u. for the model system polyhydorgen and for the other polymeric chains.

9.9 Appendix: Periodic implementation

Our successful implementation of TDDFT for solids can be found in Chapter 4. The benchmarking results of this method for a large range of nonmetallic crystals, together with the incorporation, and results, of relativistic effects in TDDFT are compiled in the Chapters 5-8. Here we very briefly reconsider the the integration over the Irreducible wedge of the Brillouin zone (IBZ), to which the integration can be reduced because the wedges are related by symmetry, and in particular consider the implications for polymers, e.g., periodic systems with periodicity in one dimension.

9.9.1 Quadrature for the response kernels

The Kohn-Sham response functions, as given in Eq. 9.16, involve integrations over the irreducible Brillouin zone, in which the denominator can become singular. The energy dependent part is therefore separated from the rest according to

\[
I_{ia}(\omega) = \int_{V_{IBZ}} \frac{g_{ia}(\mathbf{k})}{\omega - (\epsilon_{ak} - \epsilon_{ik}) + i\eta} d\mathbf{k} = \int_{\epsilon_0}^{\epsilon_1} \frac{g_{ia}(\epsilon)}{\omega - \epsilon + i\eta} d\epsilon,
\]  

(9.24)

in which \( g_{ia}(\epsilon) = \int d\mathbf{k} g_{ia}(\mathbf{k}) \delta(\epsilon - (\epsilon_{ak} - \epsilon_{ik})) \), and \( \epsilon_0, \epsilon_1 \) are the minimum and maximum value of \( \epsilon(\mathbf{k}) \) occurring in \( V_{IBZ} \). For the integration in Eq. 9.24 accurate quadrature schemes exist (Ref. [48]) which give us the weights \( \tilde{w}_{iakj}(\epsilon) \), such that

\[
g_{ia}(\epsilon) = \sum_j \tilde{w}_{iakj}(\epsilon) g_{ia}(\mathbf{k}_j).
\]  

(9.25)
In the linear tetrahedron scheme these weights are piecewise cubic polynomials in $\epsilon$.

For the quadrature of Eqn. 9.24 we can write

$$I_{ia}(\omega) = \int_{\epsilon_0}^{\epsilon_1} \frac{g_{ia}(\epsilon)}{\omega - \epsilon + i\eta} d\epsilon = \sum_j w_{iak_j}(\omega)g_{ia}(k_j).$$  \hspace{1cm} (9.26)$$

We only have to integrate the weights $\tilde{w}_{iak_j}(\epsilon)$ in the following way to obtain the new weights $w_{iak_j}(\omega)$ as functions of $\omega$,

$$w_{iak_j}(\omega) = \int_{\epsilon_0}^{\epsilon_1} \frac{\tilde{w}_{iak_j}(\epsilon)}{\omega - \epsilon + i\eta} d\epsilon = \mathcal{P} \int_{\epsilon_0}^{\epsilon_1} \frac{\tilde{w}_{iak_j}(\epsilon)}{\omega - \epsilon} d\epsilon + i\pi \tilde{w}_{iak_j}(\omega).$$  \hspace{1cm} (9.27)$$

The real and imaginary parts of this weight can thus be obtained separately using the Cauchy principle value and residual parts.

### 9.9.2 Integrations in the IBZ

Two algorithms are generally used (depending on the energy dispersion in the energy bands) for the calculation of the integration weights, $w_{iak_j}(\omega)$, as given in Eqn. 9.27.

1. **Energybands with dispersion**

For the integration of Eq. 9.26, the parameterization inside the tetrahedrons (3D) or triangles (2D), in which the IBZ is divided, is the same as given in Ref. [48]. In the general (3D case), $g_{ia}(k)$ is found by linear interpolation inside the tetrahedron by

$$g_{ia}(k) = g_{ia}(k_x, k_y, k_z) = g_1 + g_2k_x + g_3k_y + g_4k_z.$$  \hspace{1cm} (9.28)$$

Thus the contributions from a simplex S become

$$\int_S g_{ia}(k) \omega - \epsilon + i\eta d\mathbf{k} = \sum_{i=1}^{4} g_i I_i,$$  \hspace{1cm} (9.29)$$

in which the coordinate transformation from Cartesian $(k_x, k_y, k_z)$ to internal coordinates, parametrizing the constant energy surface, $(e, u, v)$ is made, and when writing $\mu_i = 1, k_x, k_y, k_z$ and $e = \omega - \epsilon$; $I_i$ in Eqn. 9.29. is calculated from

$$I_i = \int_{\epsilon_0}^{\epsilon_1} de \int_{0}^{1} du \int_{0}^{1-u} dv \left[\frac{\mu_i}{e + i\eta} \cdot \frac{\delta(k_x, k_y, k_z)}{\delta(e, u, v)}\right].$$  \hspace{1cm} (9.30)$$

The numerical integration weights $w_{iak_j}(\omega)$ are then directly calculated from $I_i$ as described in Appendix 2. from Ref. [48].
2. Energybands without dispersion

The term
\[
\frac{1}{\omega - (\epsilon_{ak} - \epsilon_{ik}) + i\eta},
\]
in Eqn. 9.24. becomes \(k\) independent, and can be placed outside the integral over \(k\). When writing \(\Delta = \omega - (\epsilon_{ak} - \epsilon_{ik})\) as the average value in the tetrahedron, the integral of Eqn. 9.29. takes the form
\[
\frac{1}{\Delta + i\eta} \int g_{ia}(k) \, dk.
\]

Also using linear interpolation for \(g_{ia}(k)\) in this case, but now making the coordinate transformation \(\delta(k_x, k_y, k_z)/\delta(k_x, u, v)\) (in the 3D case again). Results for the integrals \(I_i\) of Eqn. 9.29 in
\[
I_i = \frac{1}{1 - i\eta} \int_{k_{x,\text{min}}}^{k_{x,\text{max}}} \, dk_x \int_{0}^{1} \, du \int_{0}^{1-u} \, dv \left[ \mu_i \delta(k_x, k_y, k_z) \right]
\]

9.9.3 Crystals, surfaces, and polymers

The irreducible Brillouin zone is subdivided into tetrahedrons in the three dimensional case (crystals). The tetrahedrons are identified by 4 \(k\)-points in the reciprocal space. For the two dimensional case (surfaces), the IBZ reduces to triangles which can be indentified by 3 \(k\)-points. For polymers, the one dimensional case, the IBZ is subdivided into lines. The lines are indentified by 2 \(k\)-points in the reciprocal space. In these 2 \(k\)-points, the \(x\)-coördinates and also the energy \(\epsilon_{n,k}\) of the \(n\) energy bands are known from the DFT groundstate calculation. The integral in Eq. 9.30, in case the energybands show dispersion, reduces in the one dimension case to
\[
I_i = \int_{\epsilon_0}^{\epsilon_1} \, d\epsilon \left[ \frac{\mu_i}{\epsilon} \cdot \frac{\partial k_x}{\partial \epsilon} \right],
\]
in which \(\epsilon_1 = \omega - (\epsilon_{a,k_1} - \epsilon_{i,k_1})\) for that specific occupied \((i)\), virtual \((a)\) combination in \(k_1\). The \(k\)-points have been ordered on the values of \(\epsilon\). Only one case needs to be considered in which \(\epsilon_1 < \epsilon < \epsilon_2\). The intersection of \(\epsilon\) with the line is just a point for which
\[
k = k_1 + \frac{\epsilon - \epsilon_1}{\epsilon_2 - \epsilon_1} (k_2 - k_1),
\]
and
\[
\frac{\partial k_x}{\partial \epsilon} = \frac{1}{(\epsilon_2 - \epsilon_1)} [k_{2x} - k_{1x}].
\]

At most, this parameterization for evaluating the integrals \(I_i\) in Eq. 9.34 gives us a linear term in \(\epsilon\). In case the energybands show no dispersion the integral in Eq. 9.33 reduces to
\[
I_i = \frac{1}{\Delta + i\eta} \int_{k_{x,\text{min}}}^{k_{x,\text{max}}} \, dk_x [\mu_i]
\]
The integration over $\epsilon$ is not necessary, and is just over the x-coördinate of the $k$-points. These integrals become extremely simple, as can be seen directly from Eqn. 9.37.