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Static (hyper-)polarizabilities of infinite, conjugated polymers in the framework of density-functional theory

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It is shown how the effects of an external electrostatic field on infinite, conjugated polymers can be included directly in a density-functional method for electronic-structure calculations. In the simpler case that the field does not break the translational symmetry, our tests results for the H_2 molecule show that our computational method is reliable, and our results for *trans*-polyacetylene and polycarbonitrile demonstrate the effects of the presence of heteroatoms in the backbone as well as that the electronic properties change only a little upon also strong external fields. Finally, we present a method with which these fields can also be treated in the case that they break the translational symmetry of the polymer.

I Introduction

One area where conjugated polymers currently received much attention is in the field of non-linear optics. In the general case that a (finite or infinite) molecule is exposed to some external electromagnetic field $\boldsymbol{E}$, its total energy, E_{tot}, and dipole moment, $\boldsymbol{\mu}$ will change:

$$E_{\text{tot}}(\boldsymbol{E}) = E_0 - \boldsymbol{\mu}_0 \cdot \boldsymbol{E} - \boldsymbol{\alpha} : \boldsymbol{E}^2 - \boldsymbol{\beta} \vdots \boldsymbol{E}^3 \cdots \tag{1}$$

and

$$\boldsymbol{\mu}(\boldsymbol{E}) = \boldsymbol{\mu}_0 + \boldsymbol{\alpha} \cdot \boldsymbol{E} + \boldsymbol{\beta} : \boldsymbol{E}^2 \cdots + \boldsymbol{\gamma} : \boldsymbol{E}^3 \cdots \tag{2}$$

Here, $\boldsymbol{\alpha}$ is the polarizability, whereas $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, *etc.* are the first, second, *etc.* hyperpolarizabilities. All quantities are tensors, and when the field is time-dependent, so are the (hyper-)polarizabilities. Alternatively, when Fourier-transforming the time dependence and the hyperpolarizabilities $\boldsymbol{\beta}$, $\boldsymbol{\gamma}$, *etc.* are sufficiently large, a material, when exposed to a field of one or more frequencies, may respond by emitting light of new frequencies that are the sum and/or differences of the applied ones.

To optimize the materials for applications it is important to have a clear understanding of how the composition and structure of a compound influences the polarizabilities and hyperpolarizabilities. Here, theoretical studies may be of help. However, such studies are far from trivial and the current approaches can not be considered optimal. It is the purpose of the present work to present the first results of our work towards developing a new approach for calculating the (hyper-)polarizabilities of extended systems, including conjugated polymers.

The π electrons of the conjugated polymers are so loosely bound that they show large responses to external fields, but are simultaneously so strongly bound to the polymer backbone that their responses have not only large linear but also large non-linear components.

At present, polarizabilities and hyperpolarizabilities are calculated using either a perturbation-theoretical approach or a finite-field approach. With the former, use is made of the fact that the strengths of the applied electromagnetic fields as felt by the electrons and nuclei are many orders of magnitude weaker than the electrostatic fields of the nuclei and electrons (*e.g.*, the electrostatic field inside a hydrogen atom is typically $E = e/a_0^2$, corresponding to a field strength of about 10^{17} W cm^{-2} compared with typical applied fields from strong lasers of up to 10^{10} W cm^{-2}). Within this approach one can calculate the complete frequency-dependences of the (hyper-)polarizabilities. It has, however, some drawbacks whose consequences on the reliability on the results are not fully understood so that an alternative approach would be useful.

First, the perturbation method (the so-called sum-over-states, SOS, method[1,2]) involves all occupied and unoccupied orbitals and, in particular, the latter requires well-converged basis sets, which for large finite systems is difficult to achieve. Second, the polarizability should, in principle, be able to describe absorption spectra. However, the denominators of the SOS expression involve differences between single-particle energies of occupied and empty orbitals, implying that the accuracy with which the absorption threshold is described is very sensitive to that of the band gap. Here, neither Hartree–Fock- nor density-functional-based methods are reliable so that, at least when truncating the perturbation series after a finite number of terms, a wrong absorption threshold is obtained. Third, the numerators involve single-particle matrix elements for the dipole-moment operator. For infinite systems, the definition of this operator is not obvious, or, alternatively, the matrix elements may diverge (we shall return to this problem below). Instead, one usually studies finite systems of growing size, attempting to estimate the saturations of the (hyper-)polarizabilities per unit through extrapolation. That this saturation often is reached first for very large systems[3] makes this approach computationally demanding.

The finite-field-method[2,4] is used to calculate the responses of the system to external static fields. In that case, the field can be included directly in the Hamiltonian and the responses of the system calculated self-consistently for various strengths of the field. Finally, the derivatives of the dipole moment (calculated numerically) determines the static (hyper-)polarizabilities. Most often this approach is applied to finite systems; when attempting to apply it to finite systems, the problems related to the unique definition of the dipole moment as well as diverging matrix elements remain.

Currently, we are developing a formalism for calculating the static electronic (hyper-)polarizabilities per unit cell of infinite, periodic systems (we are accordingly neglecting the nuclear parts of the polarizabilities and hyperpolarizabilities although

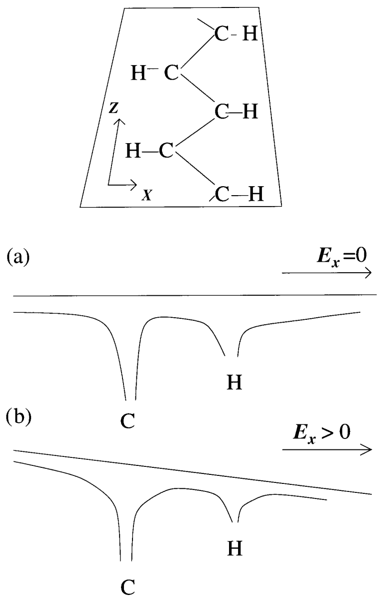

Fig. 1 Schematic representation of the single-particle potential along one of the C—H bonds for *trans*-polyacetylene as felt by an electron when (a) a vanishing and (b) a non-vanishing potential that is perpendicular to the chain is applied.

these may be non-negligible[5]). Simultaneously, we are developing the accompanying computer codes using a density-functional method. So far we have concentrated on static (DC) fields, but are planning to extend the work to time-dependent fields. The purposes of this presentation are twofold. First, we shall show that the density-functional calculations can provide accurate results also for those quantities. To this end we study cases where the applied field does not break the translational symmetry. Second, we shall present our formalism for how to deal with the case where the external field destroys the symmetry and, ultimately, may lead to diverging matrix elements.

The paper is divided as follows. In Section II we describe our density-functional method for the static case without external fields. Section III is devoted to the problems related to including these external fields, and in Section IV we present our results for an applied static field perpendicular to the chain direction of two simple conjugated polymers, *trans*-polyacetylene and polycarbonitrile. In Section V we present our formalism for how to treat the case of static fields with components parallel to the polymer axis, and in Section VI we summarize and conclude.

II Density-functional method

For the system (*i.e.*, a molecule or a polymer) without any external fields we apply a density-functional method that has been described in detail elsewhere[6–9] and, therefore, only briefly shall be presented here. Assuming that the Born–Oppenheimer approximation is valid, we seek the ground state for the electrons moving in the electrostatic field of the nuclei. According to the theorem of Hohenberg and Kohn[10] any ground-state property can be calculated as a functional of the electron density, $\rho(\boldsymbol{r})$. Unfortunately, the functional defining the total energy is unknown, but according to Kohn and Sham[11] the problem of calculating this can be reformulated as that of solving a set of single-particle equations:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}}(\boldsymbol{r})\right]\psi_j(\boldsymbol{r}) = \varepsilon_j \psi_j(\boldsymbol{r}) \tag{3}$$

with

$$V_{\text{eff}}(\boldsymbol{r}) = V_{\text{n}}(\boldsymbol{r}) + V_{\text{C}}(\boldsymbol{r}) + V_{\text{XC}}(\boldsymbol{r}) \tag{4}$$

being the sum of the electrostatic potential from the nuclei, that from the electrons, and the so-called exchange-correlation potential. In the present work we use the local approximation of von Barth and Hedin[12] for V_{xc}. The total electron density is given as the sum over the occupied single-particle orbitals

$$\rho(\boldsymbol{r}) = \sum_{j=1}^{\text{occ}} |\psi_j(\boldsymbol{r})|^2 \tag{5}$$

To solve these equations, we expand the eigenfunctions ψ_j in terms of atom-centered basis functions, $\{\chi_{\boldsymbol{R},\kappa,L}(\boldsymbol{r})\}$, where $\boldsymbol{R}$ is the position of the atom, $L \equiv (l, m)$ describes the angular dependence, and κ the radial dependence of the basis functions.

For infinite, periodic, quasi-one-dimensional systems like the conjugated polymers in the absence of an external field it is extremely useful to construct symmetry-adapted basis functions (characterized by k) from equivalent basis functions of different unit cells:

$$\chi^k_{p,\kappa,L}(\boldsymbol{r}) = \lim_{N\to\infty} \frac{1}{\sqrt{2N+1}} \sum_{n=-N}^{N} \chi_{\boldsymbol{R}_{np},\kappa,L}(\boldsymbol{r})\mathrm{e}^{\mathrm{i}k\pi n} \tag{6}$$

where $\boldsymbol{R}_{np}$ is the position of the pth atom of the nth unit cell.

With this approach, the problem of solving the $\infty \times \infty$ secular equation for the infinite system is transformed into that of solving a set (of different k) of finite secular equations whose size is that of the number of basis functions per unit cell. In the exact case, the number of k points is infinite, but sufficiently accurate results are usually obtained with a finite set of N_k equidistant k points.

In our approach, the basis functions χ are so-called muffin-tin orbitals that are represented numerically inside non-overlapping, atom-centered (muffin-tin) spheres and analytically outside of them. For the present discussion their precise form is not important, but the interested reader is referred to refs. 6 and 7 for a more detailed discussion, and to ref. 8 for applications of this approach to various polymeric systems.

III The dipole moment and the static field

For the systems of our interest, the dipole moment is defined as

$$\boldsymbol{\mu} = \sum_k Z_k e \boldsymbol{R}_k - e \int \rho(\boldsymbol{r})\boldsymbol{r}\, \mathrm{d}\boldsymbol{r} \tag{7}$$

with $Z_k e$ being the charge of the kth nucleus at $\boldsymbol{R}_k$, and $\rho(\boldsymbol{r})$ being the electron distribution. This quantity is poorly defined for extended systems. To see this we consider a simple chain of N A and B atoms each having the charge $\pm q$. With the interatomic distance being a, the dipole moment per unit parallel to the chain is $\pm qa$, depending on the atoms that terminate the chain. This leaves the impression that the dipole moment of extended systems is a surface effect. However, Vanderbilt and King-Smith[13] showed that the existence of a permanent polarization (related to a dipole moment) of an infinite crystalline system is a property dictated by the electron density of the bulk, *i.e.*, the polarization is a bulk property. They showed also that its size was only given within certain additive constants that only depend on the structure.

Their results imply that to study the dipole moment, and its variation with external field, of *e.g.*, conjugated polymers it is a valid approach to study an infinite, periodic chain. Furthermore, the static polarizabilities and hyperpolarizabilities are well-defined quantities, being the derivatives of the dipole moment with respect to the external field.

An external, electrostatic potential leads to an extra term in the Hamiltonian:

$$\hat{H}_{\text{e}} = \sum_k Z_k e\boldsymbol{E} \cdot \boldsymbol{R}_k - \sum_j e\boldsymbol{E} \cdot \boldsymbol{r}_j \tag{8}$$

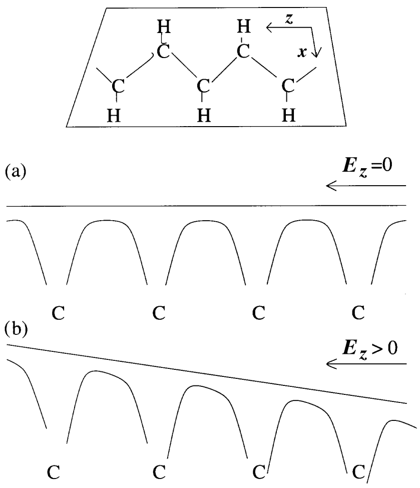

Fig. 2 As Fig. 1, but parallel to the chain axis.

where r_j is the position of the jth electron. Then, the single-particle operator of eqn. (3) is to be extended by the term

$$\hat{h}_e = -e\boldsymbol{E} \cdot \boldsymbol{r} \tag{9}$$

When including this operator directly into the Hamiltonian and studying the response of the dipole moment on the external field, only ground state properties are calculated, which ensures that electronic-structure methods based on Hartree–Fock or density functional approaches can be applied.

For the infinite polymer we may now distinguish between two fundamentally different situations. Either (Fig. 1) the applied field has no component parallel to the chain axis, or (Fig. 2) that component is non-vanishing. In Fig. 1 and 2 we have sketched the changes in the single-particle potential felt by the electrons when applying an external field for the prototype of the conjugated polymers, *trans*-polyacetylene.

In the first case, Fig. 1, the potential along the C—H bonds pointing to the left will be different from that along the bonds to the right. However, the translational symmetry remains, and one can directly include the effects of the external field in the calculations and solve these as described in the previous section.

In the second case, Fig. 2, the translational symmetry is destroyed, the functions of eqn. (6) are no longer symmetry-adapted basis functions, and k is not a good quantum number. One may still use these functions as basis functions, but, then, functions of different k will have non-vanishing matrix elements with the operator of eqn. (9). Furthermore, that operator diverges for $z \to \pm\infty$, making the matrix elements ill-defined.

To circumvent this problem, one may attempt to restore the symmetry. This was done, *e.g.*, by Otto[14] who only included that part of the operator that has the same periodicity as the undistorted system. We believe that this is too crude an approximation, and shall below present our proposal. But first we shall study the effects of an external field as calculated with our density-functional method by considering the simpler case of Fig. 1.

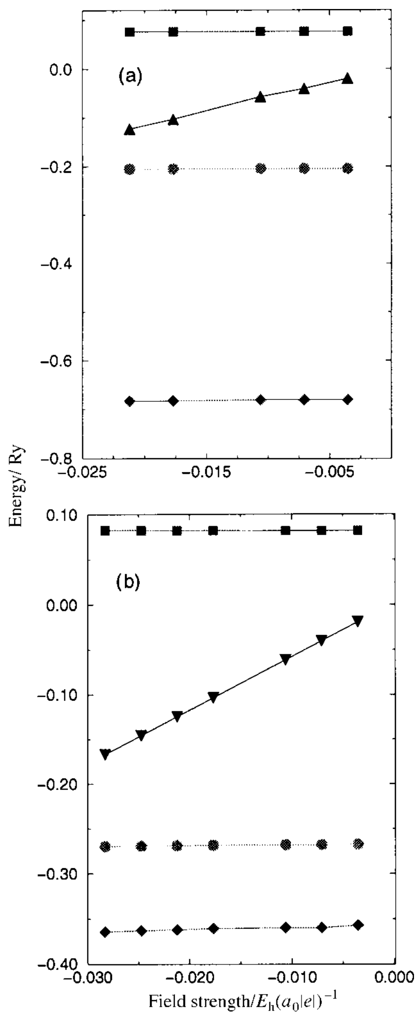

Fig. 3 Changes in the total energy (◆), the Fermi energy (●), the band gap (■), the y component of the dipole moment (▲), and the x component of the dipole moment (▼) for *trans*-polyacetylene as functions of field strengths for the field parallel to (a) the y-axis and (b) the x-axis. All quantities are given in Rydberg atomic units.

IV The field perpendicular to the chain

To test the reliability of the present computational scheme, we studied an isolated H_2 molecule and the two conjugated polymers *trans*-polyacetylene (*cf.* Fig. 1 and 2) and polycarbonitrile (obtained from *trans*-polyacetylene upon replacing every second CH group by an N atom). A short account of that work was published recently,[15] but here we shall present a more thorough analysis.

We include the effects of the external field directly in the Hamiltonian. Subsequently, for various directions [in the (x, y) plane] and strengths of the external field we calculate the total energy and the components of the dipole moment perpendicular to the chain axis. These are finally fitted to a polynomial in the field strengths, from which the static polarizabilities and hyperpolarizabilities can be extracted. In this approach, the strengths of the external fields are not chosen according to experimental criteria but rather as a means of obtaining the desired information. However, although the strengths often are somewhat larger than what is experimentally possible at the moment, they should not be so large that the electronic distributions are strongly affected by their presence.

The H_2 molecule is so small that it can be examined with highly accurate methods. In particular, Mosley *et al.*[16] have presented results of calculations of the polarizabilities of a single, isolated molecule using various computational schemes, including Hartree–Fock and density-functional-based ones. They found static polarizabilities along the bond of 5.812, 10.852, 11.312 and 12.311 $(a_0|e|)^2/E_h$ when using STO-3G, 3-21G, 6-31G** and 6-311G* basis sets, respectively, in the density-functional calculations.

Repeating periodically a H_2 molecule with the bond axis perpendicular to the polymer axis and an intermolecular distance of 50 a_0 we obtained a value of 9.69 $(a_0|e|)^2/E_h$, which is in reasonable agreement with the results of Mosley *et al.* for better basis sets. Both in their and in our calculations the bond length was set equal to 2 a_0.

Subsequently, we studied the two conjugated polymers mentioned above. For *trans*-polyacetylene the C—C bond lengths were set equal to 2.58 and 2.67 a_0 and the C—C—C bond angles to 128°, as has been found previously.[7] Equivalently, the C—N bond lengths of polycarbonitrile were chosen as 2.54 and 2.67 a_0, and the C—N—C and N—C—N bond angles as 122°.[17]

In Fig. 3 and 4 we show the variation of some of the key quantities for the two systems as functions of the field strengths. It is seen that the quantities do depend on the field, but also that for experimentally realistic strengths (of the order of 10^{-6} $E_h/a_0|e|^{-1}$), the changes in the electronic properties are marginal. This is also seen in Fig. 5 where we show the band structures and the highest occupied orbital (at $k = 0$) for polycarbonitrile for different strengths of the field. Polycarbonitrile is somewhat atypical by having a σ band (due to N lone-pair orbitals) defining the top of the valence bands, but the similarities between the results of Fig. 3 and 4 suggests that the behaviour in Fig. 5 is general.

When fitting the density-functional results with polynomials we obtained the values of Table 1. Due to the inversion symmetry of *trans*-polyacetylene, $\boldsymbol{\beta}$ vanishes, which is not the case for polycarbonitrile. Furthermore, the presence of the heteroatom (N) for polycarbonitrile makes the polarizability along the x-axis of this compound larger than for polyacetylene, whereas the opposite is the case for the polarizability along the y-axis.

Only a few theoretical studies have been made of some of these quantities. Experimentally, it is not possible to separate the contribution from the electrons and the nuclei, and, therefore, we shall here concentrate on a comparison with theoretical results. For *trans*-polyacetylene, Champagne *et al.*[18] found static polarizabilities of $\alpha_{xx} = 25.5$ and $\alpha_{yy} = 9.5$ $(a_0|e|)^2/E_h$, which is in fair agreement with our values, except for the sign of the latter. In a later work on polycarbonitrile, Champagne and co-workers[19] showed that the static polarizabilities and hyperpolarizabilities are very sensitive to the precise structure of the system, which may be the reason for the deviations above. In that work, they reported β_{xxx} around 35–40 $(a_0|e|)^3/E_h{}^2$ for polycarbonitrile. These values were obtained by extrapolating *ab initio* Hartree–Fock results for finite oligomers with up to 20 formula units. In an earlier work[20] they found, on the other hand, values between 0.3 and 6.3 $(a_0|e|)^3/E_h{}^2$ when using various parametrized methods for finite oligomers. In total we see that our values compare favourably with the *ab initio* values when taking into account the number of uncertainties to which these quantities are subject.

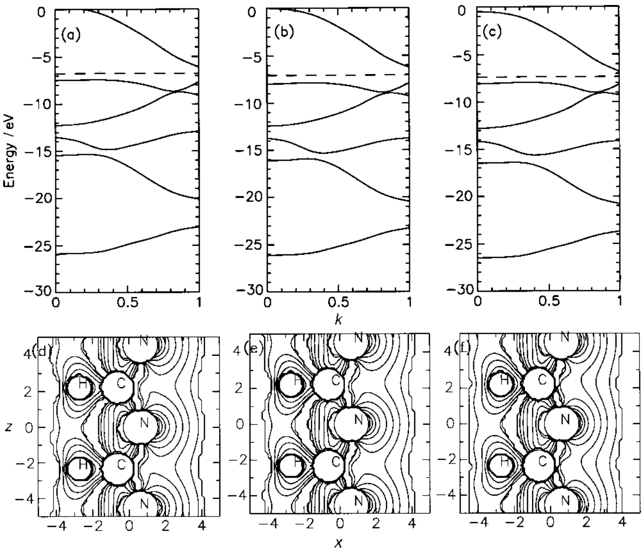

Fig. 5 The band structures (top) and the electron density for the highest occupied orbital (at $k = 0$) outside the muffin-tin sphere (bottom) for polycarbonitrile when exposed to an external DC-field of (left) − 0.05, (middle) 0.0, and (right) 0.05 $E_h/|e|a_0$ along the x-axis.

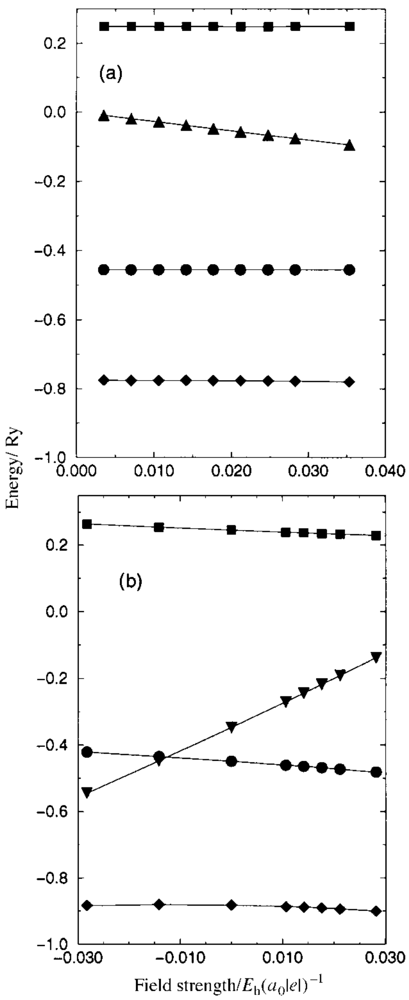

Fig. 4 As Fig. 3, but for polycarbonitrile.

V The field parallel to the chain

The results of the previous section show that the current density-functional method can be applied in calculating static

Table 1 Calculated static dipole moments, static polarizabilities, and static hyperpolarizabilities for *trans*-polyacetylene and polycarbonitrile; all values are given in Rydberg atomic units

Parameter	$(CHN)_x$	$(CH)_x$
$\mu_{0,x}$	−0.79	0.0
$\mu_{0,y}$	0.0	0.0
α_{xx}	−19.2	−16.5
α_{yy}	−7.4	−14.8
α_{xy}, α_{yx}	0.2	0.3
β_{xxx}	20.0	0.0
β_{yyy}	8.0	0.0
$\beta_{xxy} + \beta_{xyx}$	0.0	0.0
$\beta_{yyx} + \beta_{yxy}$	−7.0	0.0
γ_{xxxx}	−4.0	4.12
γ_{yyyy}	−93.0	86.0
$\gamma_{xxxy} + \gamma_{xxyx} + \gamma_{xyxx} + \gamma_{xxyy} + \gamma_{xyxy} + \gamma_{xyyx}$	12.0	−319.0
$\gamma_{yyyx} + \gamma_{yyxy} + \gamma_{yxyy} + \gamma_{yyxx} + \gamma_{yxyx} + \gamma_{yxxy}$	135.0	−42.0

polarizabilities and hyperpolarizabilities for polymeric systems. Furthermore, these quantities can be calculated by applying a finite-field method with field strengths that still are larger than the experimentally realizable ones but nevertheless so small that the changes in the electronic orbitals and their energies are very modest. The last point implies that the electronic eigenfunctions for the undistorted system form a good basis for studying the system when it is exposed to the external fields. We shall now use this observation to develop a new approach for calculating the static (hyper-)polarizabilities along the chain direction.

For the unperturbed system, the eigenfunctions to the Kohn–Sham equation [eqn. (3)] are written as linear combinations of the Bloch waves [eqn. (6)] for a specific k. This means that they are delocalized over the complete system, so that the matrix elements for these with the operator of eqn. (9) are ill-defined.

As mentioned in Section II, the Bloch waves ψ_l^k are calculated not for the complete (infinite) set of k values but only for N_k equidistant ones. From the N_k Bloch waves of a specific band (characterized by l) we construct N_k Wannier functions:

$$w_{l,p}(\boldsymbol{r}) = \frac{1}{\sqrt{N_k}} \sum_k \psi_l^k(\boldsymbol{r}) \cdot \mathrm{e}^{\mathrm{i}\bar{\phi}(k)}\, \mathrm{e}^{\mathrm{i}kp} \tag{10}$$

Here, $\mathrm{e}^{\mathrm{i}\bar{\phi}(k)}$ is a k-dependent phase factor that can be chosen freely. It reflects the fact that the single-particle eigenfunctions ψ_l^k contain an arbitrary phase factor.

The function $w_{l,p}$ in eqn. (10) is periodic with the periodicity of the Born-von Kármán zone:

$$w_{l,p}(\boldsymbol{r} + L \cdot z) = w_{l,p}(\boldsymbol{r}) \tag{11}$$

with

$$L = N_k \cdot a \tag{12}$$

where a is the length of one unit cell, and $\boldsymbol{z}$ is a unit vector in the z direction.

By appropriate choice of the phase factors and for sufficiently large N_k, the Wannier function $w_{l,p}$ is localized close to the pth unit cell. Thus, in the limit of an infinite set of k points, the Wannier functions constitute a set of localized functions that, moreover, contain exactly the same information as the original Bloch waves. Finally, the Wannier functions are orthonormal, and changing p by 1 leads to a new Wannier function that is identical with the original one except for being displaced by one unit cell. Thus, in our approach we shall use Wannier functions calculated from the Bloch waves of the system in the absence of the external field as basis functions in studying the system exposed to the external field. Thereby we have a basis set of localized functions that contains the maximum information from the unperturbed system and whose size is reasonably small. In an actual calculation we will use the Wannier functions of all the occupied valence bands as well as those of the lowest unoccupied conduction bands.

One of the open questions is that of specifying the phase factors in eqn. (10). Appropriately chosen they lead to a maximum localization of the Wannier functions, although it is a far from trivial task to do so.[21–24] Our preliminary results indicate that one should be very careful at this point, and that Wannier functions that appear to be localized to one unit cell and to have small components in the nearest-neighbouring unit cells may very well have larger components in slightly more distant unit cells. This point has not been addressed previously.

The other reformulation we shall make is that of the z-component of the operator of eqn. (9). Explicitly written, we have

$$\hat{h}_e = -e(E_x x + E_y y + E_z z) \to -e(E_x x + E_y y + E_z \hat{z}) \tag{13}$$

In a typical calculation where the infinite set of k points is replaced by a finite set of equidistant points, it is indirectly assumed that the system possesses the periodicity of the Born-von Kármán zone, eqn. (11), as also has been pointed out by Resta.[25] To be internally consistent it is therefore important that the operator of eqn. (13) also possesses this periodicity. Resta[25] has presented one proposal for such a operator that, however, contains spurious many-electron terms. Our proposal does not include such dependences:

$$\hat{z} = \sum_m \hat{z}_m \tag{14}$$

with the sum running over all Born-von Kármán (BvK) zones. Furthermore,

$$\hat{z}_m = \begin{cases} z - m \cdot L & \text{in the } m\text{th BvK zone} \\ 0 & \text{otherwise} \end{cases} \tag{15}$$

This operator has the advantage that, in the limit of an infinite number of k points, it converges to the correct operator, in contrast to the proposal of Otto.[14]

With the Wannier functions of eqn. (10) (including an optimization of their localization through appropriate choice of the phase factors) and the single-particle operators of eqn. (13)–(15), the problem of calculating the static polarizabilities and hyperpolarizabilities is transformed into that of solving the single-particle Kohn–Sham equations:

$$\hat{H}_{\text{eff}}\, \psi_j(\boldsymbol{r}) = \varepsilon_j \psi_j(\boldsymbol{r}) \tag{16}$$

with

$$\begin{aligned}\hat{H}_{\text{eff}} &= \hat{H}^0_{\text{eff}} - eE_z \hat{z} \\ &= \left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(\boldsymbol{r}) - e(E_x x + E_y y) \right] - eE_z \hat{z} \end{aligned} \tag{17}$$

The solutions ψ_j are expanded in the Wannier functions:

$$\psi_j(\boldsymbol{r}) = \sum_{l,p} c_{j,l,p}\, w_{l,p}(\boldsymbol{r}) \tag{18}$$

All basis functions, potentials, *etc.* are per construction periodic with the BvK zones, and one needs therefore only a minimal set of them.

Solving the above equations leads to a secular equation involving the Hamiltonian matrix elements:

$$\begin{aligned}&\langle w_{l_1,p_1} | \hat{H}_{\text{eff}} | w_{l_2,p_2} \rangle \\ &\quad = \langle w_{l_1,p_1} | \hat{H}^0_{\text{eff}} | w_{l_2,p_2} \rangle - \langle w_{l_1,p_1} | eE_z \hat{z} | w_{l_2,p_2} \rangle \end{aligned} \tag{19}$$

In the first term on the right-hand side, the operator has the periodicity of the underlying lattice (*i.e.*, not that of the BvK zones), and the matrix elements are therefore best evaluated using the representation of the Wannier functions in terms of the Bloch waves, eqn. (6).

The second term is best evaluated using the Wannier functions directly. It can be rewritten so that it involves only an integration over one unit cell (not the full BvK zone–the details of this shall not be presented here), and can then be performed, *e.g.*, numerically. When the Wannier functions are well localized, only a few terms need to be calculated.

Finally, the secular equation also includes the overlap matrix of the Wannier functions, which, however, is the unit matrix due to the fundamental properties of the Wannier functions.

We have implemented the above ideas using a computational scheme similar to that of the previous sections. The first test calculations indicate that the scheme is working. Repeating the test calculations for a H_2 molecule with the present approach gave a static polarizability of 11.85 $(a_0|e|)^2/E_h$. Since the polarizability is very sensitive to the calculational method and the basis set, this value compares well with the values quoted in the preceding section.

VI Conclusions

The purpose of this contribution has been twofold. First, we have shown that our density-functional method can be applied in studying static polarizabilities and hyperpolarizabilities of polymeric systems, including conjugated polymers. Second, we have presented a formalism, not restricted to density-functional methods, with which the effects of the electrostatic field can also be included directly in calculations for the infinite system when the field breaks the translational symmetry.

Our aim has been to abandon the currently applied approximations such as a perturbation expansion with a not-converged basis set, or those of extrapolating results for finite systems to the limit of infinite systems. Since these approximations often have largely unknown effects on the finite results, it is of importance to be able to calculate the quantities with alternative methods like the one we are proposing here.

When the field is perpendicular to the polymer axis, its effects can fairly easily be included directly in the calculations. We showed that, in doing so, our computational scheme produces reliable results for a simple test case, the H_2 molecule. For two simple conjugated polymers, *trans*-polyacetylene and polycarbonitrile, we presented the static polarizabilities and hyperpolarizabilities and showed that the currently accessible experimental fields lead to only very modest changes in the electronic orbitals and energies. This implies that a perturbation-theoretical expansion is well justified, and also that the wavefunctions for the unperturbed system form a good starting point in studying the effects of the electrostatic field.

We used the latter when developing our formalism for treating the case that the field has a component parallel to the polymer axis. From the Bloch waves of the unperturbed system we formed Wannier functions that should be chosen according to a criterion of maximum localization. Furthermore, our $\hat{z}$ operator was chosen so that it, as for the Wannier functions, was periodic with the BvK zone. This leads to an internally consistent approach for calculating the static (hyper-)polarizabilities that, in addition, can be made arbitrarily accurate upon increasing the number of k points.

The accompanying computer codes are not fully developed and, therefore, we abandoned any representation of results for conjugated polymers obtained with this scheme. Finally, we note that our approach should also have relevance for the calculation of the spontaneous polarization in dielectrics, which should represent a simpler problem since 'only' the dipole moment in the absence of a field is sought.

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References

1 V. M. Genkin and P. M. Mednis, *Sov. Phys. JETP*, 1968, **27**, 609.
2 J.-M. André, J. Delhalle and J.-L Brédas, *Quantum Chemistry Aided Design of Organic Polymers*, 1991, World Scientific, Singapore.
3 I. D. W. Samuel, I. Ledoux, C. Dhenaut, J. Zyss, H. H. Fox, R. R. Schrock and R. J. Silbey, *Science*, 1994, **265**, 1070.
4 H. D. Cohen and C. C. J. Roothaan, *J. Chem. Phys.*, 1965 **43**, 534.
5 B. Champagne, H. Vanderhoeven, E. A. Perpète and J. M. André, *Chem. Phys. Lett.*, 1996, **248**, 301.
6 M. Springborg and O. K. Andersen, *J. Chem. Phys*, 1987, **87**, 7125.
7 M. Springborg, J.-L. Calais, O. Goscinski and L. A. Eriksson, *Phys. Rev. B*, 1991, **44**, 12713.
8 M. Springborg, in *Density-Functional Methods in Chemistry and Materials Science*, ed. M. Springborg, Wiley, Chichester, 1997, p. 207.
9 M. Springborg, unpublished work.
10 P. Hohenberg and W. Kohn, *Phys. Rev. B*, 1964, **136**, 864.
11 W. Kohn and L. J. Sham, *Phys. Rev. A*, 1965, **140**, 1133.
12 U. von Barth and L. Hedin, *J. Phys. C*, 1972, **5**, 1629.
13 D. Vanderbilt and R. D. King-Smith, *Phys. Rev. B*, 1993, **48**, 4442.
14 P. Otto, *Phys. Rev. B*, 1992, **45**, 10876.
15 K. Schmidt and M. Springborg, *Synth. Methods*, 1997, **85** 1119.
16 D. H. Mosley, B. Champagne and J.-M. André, *Int. J. Quant. Chem., S*, 1995, **29**, 117.
17 M. Springborg, *Ber. Bunsenges. Phys. Chem.*, 1991, **95**, 1238.
18 B. Champagne, E. A. Perpète and J.-M. André, *J. Chem. Phys.*, 1994, **101**, 10796.
19 B. Champagne, D. Jacquemin, J.-M André and B. Kirtman, *J. Phys. Chem. A*, 1997, **101**, 3158.
20 D. Jacquemin, B. Champagne, J.-M. André and B. Kirtman, *Chem. Phys. Lett.*, 1996, **213**, 217.
21 E. I. Blount, *Solid State Phys.*, 1962, **13**, 305.
22 S. Suhai, Quantenmechanische Untersuchungen an Quasi-eindimensionalen Festkörpern Habilitationsschrift, Universität Erlangen-Nünberg, 1983.
23 J. J. Ladik, *Quantum Theory of Polymers as Solids*, Plenum Press, New York, 1988, p. 189.
24 N. Marzari and D. Vanderbilt, *Phys. Rev. B*, 1997, **56**, 12847.
25 R. Resta, *Phys. Rev. Lett.*, 1998, **80**, 1800.

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