PHYSICAL REVIEW B VOLUME 45, NUMBER 19 15 MAY 1992-I

Calculation of the polarizability and hyperpolarizabilities of periodic quasi-one-dimensional systems

P. Otto

Friedrich-Alexander-University Erlangen-Nürnberg, Egerlandstrasse 3, D-8520 Erlangen, Federal Republic of Germany

(Received 20 June 1991; revised manuscript received 1 October 1991)

The operator of a homogeneous electric field acting on a periodic quasi-one-dimensional system can be decomposed into a sum of two terms. One term affects interband mixing of states with the same quasimomentum **k** and therefore describes the polarization of the electronic distribution due to the electric field. The second part causes a change in the quasimomentum **k** and hence is responsible for the acceleration of the electrons. While this latter term of the potential is divergent, the first term is invariant under a translational symmetry operation. This property is used to derive a homogeneous non-Hermitian system of equations to calculate the energy bands and the crystal orbitals of the periodic infinite chain in the presence of the electric field. The system of equations is solved with the help of an iterative self-consistent-field procedure. The occurrence of numerical problems, e.g., the band crossing and the undetermined phase factor of the Bloch function, is discussed and ways in which they can be solved are indicated. Finally, the method is applied to calculate the elements of the (hyper)polarization tensors, using as input the induced dipole moment which can be computed as a function of the electric-field strength. To test the method and to select the appropriate numerical procedures, applications have been peformed for infinite chains of hydrogen, water, and lithium hydride molecules. The results of these model calculations are compared with the corresponding studies on finite molecular clusters and investigations reported in the literature.

I. INTRODUCTION

Since the time when it was shown, originally for polyacetylene,[1] that organic polymers have nonlinear optical responses of the same order of magnitude as inorganic semiconductors, theoretical interest has increased rapidly in the investigation of those properties of these systems, namely the polarizability and the hyperpolarizabilities, which are responsible for the physical behavior. The primary goals of the theoretical research are to achieve not only an interpretation of the experimental facts, but also the prediction and the design of chemical compounds with improved properties. It turns out that systems with conjugated hydrocarbon chains are the most promising ones for applications in nonlinear optics and optoelectronics.[2]

In the past, several different theoretical and computational methods have been developed and applied to a variety of organic polymers that have a conjugated backbone as the common structural feature. The most serious theoretical problem arises from the fact that the operator representing the potential of the electric field (as it is used in the finite field approach for molecules) acting on a polymer is unbounded and consequently the translational symmetry of the system will be destroyed. Therefore relatively few methods have been worked out starting from the infinite system. With the help of a perturbation-theoretical ansatz,[3] the nonlinear optical properties of conjugated polymers[4] have been treated in the tight-binding approximation. Recently this method has been extended to the *ab initio* Hartree-Fock crystal orbital level.[5] Although a fundamental computational method for accurate calculations has been derived,[6] its application to systems with large elementary cells has been forbidden until now due to the very great computational requirements.[7] Recently another approach has been proposed[8] where the unboundedness of the electric-field operator is circumvented in a different way. In the case of a weak electric field whose direction coincides with the polymer axis, one can perform several crystal orbital calculations for periodic systems, assuming different but constant potentials caused by the electric field. To obtain the properties of the perturbed total system, one has to average over polarizabilities resulting from various energy-band-structure calculations. The overwhelming number of numerical investigations has been performed on finite molecular clusters. This approach offers the possibility to extrapolate the values of the linear, second- and third-order susceptibilities for the infinite chain from clusters with increasing numbers of molecular units. Within this context, the finite field approach[9] or the sum-over-states method[10] is applied in most of the investigations.[11]

In this work, a different theoretical approach will be presented to investigate, at the *ab initio* Hartree-Fock level, the polarization of the electronic distribution in a periodic polymer due to the presence of a homogeneous electric field. The direction of the electric field is taken to be parallel to the polymer axis. The basic idea behind this theory is that the unbounded electric-field operator can be partitioned into one term that represents the polarizing effect of the electric field without destroying the periodicity of the infinite chain, and another one that describes the acceleration of the electrons under the influence of the electric field. As this method takes into account only the first term, one can investigate the perturbed polymer, taking advantage of the translational periodicity of the system. However, a time-dependent formalism has to be used if the total operator of the electric field is to be considered. The polarized Bloch function obtained in the first step can then be used for an ansatz of the time-dependent wave function.

In the next section the basic concept of the present theory will be described, first the general method and second its implementation into the Hartree-Fock crystal orbital formalism. The following part deals with difficulties that may occur in the course of the numerical solution. This section is followed by the description of the method to calculate the elements of the tensors for the (hyper)polarizability, starting from the induced dipole moment as a function of the electric-field strength. Then we will report results of the application of the theory on model chains built up by hydrogen, water, and lithium hydride molecules.

II. METHODOLOGY

A. General formalism

The total Hamiltonian $\hat{H}$ of the polymer in the presence of a constant electric field can symbolically be written in the form that is formally identical with the operator in the finite field approach,

$$\hat{H}=\hat{H}_0-\mathbf{F}\cdot\mathbf{r}\ , \tag{1}$$

where $\mathbf{F}$ is the force of the electric field $\mathbf{E}$ acting on the electron

$$\mathbf{F}=e\mathbf{E} \tag{2}$$

and $\hat{H}_0$ is the Hamiltonian of the unperturbed periodic infinite system. It is easy to verify that for the gradient of the Bloch function $\varphi_n^{\mathbf{k}}(\mathbf{r})$

$$\varphi_n^{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_n^{\mathbf{k}}(\mathbf{r}) \tag{3}$$

with respect to $\mathbf{k}$, where $u_n^{\mathbf{k}}(\mathbf{r})$ is the periodic part, the equality holds:

$$\begin{aligned}\nabla_{\mathbf{k}}\varphi_n^{\mathbf{k}}(\mathbf{r})&=i\mathbf{r}\varphi_n^{\mathbf{k}}(\mathbf{r})+e^{i\mathbf{k}\cdot\mathbf{r}}\nabla_{\mathbf{k}}u_n^{\mathbf{k}}(\mathbf{r})\\&=i\mathbf{r}\varphi_n^{\mathbf{k}}(\mathbf{r})+e^{i\mathbf{k}r\cdot\mathbf{r}}\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\varphi_n^{\mathbf{k}}(\mathbf{r})\ .\end{aligned} \tag{4a}$$

After multiplying both sides of Eq. (4a) by $-ie\mathbf{E}$ and reordering the terms, the perturbed total Hamilton operator [Eq. (1)] can be expressed as

$$\begin{aligned}-e\mathbf{E}\cdot\mathbf{r}\varphi_n^{\mathbf{k}}(\mathbf{r})=&-ie\mathbf{E}e^{i\mathbf{k}\cdot\mathbf{r}}\cdot\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\varphi_n^{\mathbf{k}}(\mathbf{r})\\&+ie\mathbf{E}\cdot\nabla_{\mathbf{k}}\varphi_n^{\mathbf{k}}(\mathbf{r})\ .\end{aligned} \tag{4b}$$

Substituting Eq. (4b) into Eq. (1), the total Hamiltonian $\hat{H}$ can be rewritten in the form

$$\begin{aligned}\hat{H}&=\hat{H}_0-ie\mathbf{E}e^{i\mathbf{k}\cdot\mathbf{r}}\cdot\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}+ie\mathbf{E}\cdot\nabla_{\mathbf{k}}\\&=\hat{H}_F+ie\mathbf{E}\cdot\nabla_{\mathbf{k}}\ ,\end{aligned} \tag{5}$$

where it is seen by inspection that $\hat{H}_F$ is defined as

$$\hat{H}_F=\hat{H}_0-ie\mathbf{E}e^{i\mathbf{k}\cdot\mathbf{r}}\cdot\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\ . \tag{6}$$

The Hamiltonian $\hat{H}_F$ takes the polarization effect of the electric field into account and is invariant under a lattice transformation because the term in $e\mathbf{E}$ does not mix states with different values of $\mathbf{k}$ but only those of different bands with the same value of $\mathbf{k}$. It can be shown that that if $\varphi_n^{\mathbf{k}}(\mathbf{r})$ are the eigenstates of $\hat{H}_0$, then

$$\begin{aligned}&-ie\left\langle\varphi_m^{\mathbf{k}'}(\mathbf{r})\left|e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{E}\cdot\nabla_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{r}}\right|\varphi_n^{\mathbf{k}}(\mathbf{r})\right\rangle\\&\qquad=-ie\int d\mathbf{r}e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}}u_m^{\mathbf{k}'}(\mathbf{r})\mathbf{E}\cdot\nabla_{\mathbf{k}}u_n^{\mathbf{k}}(\mathbf{r})\ ,\end{aligned} \tag{7}$$

which vanishes except for $\mathbf{k}=\mathbf{k}'$ because the term $u_m^{\mathbf{k}'}(\mathbf{r})\nabla_{\mathbf{k}}u_n^{\mathbf{k}}(\mathbf{r})$ is invariant under a lattice transformation. This means that $\hat{H}_F$ affects interband mixing and only the divergent term $ie\mathbf{E}\cdot\nabla_{\mathbf{k}}$ in Eq. (5) can cause a change of the quasimomentum $\mathbf{k}$ (Ref. 12), which would destroy the periodicity of the chain.

The definition of the translational invariant operator $\hat{H}_F$ [Eq. (6)] is used to calculate the energy-band structure of the periodic system perturbed by the electric field. With the help of the variational principle one can derive (as in the case of molecules) the expression for the Fock equation in $\mathbf{k}$ space:

$$\hat{F}_F^{\mathbf{k}}\varphi_n^{\mathbf{k}}(\mathbf{r})=\varepsilon_n^{\mathbf{k}}\varphi_n^{\mathbf{k}}(\mathbf{r})\ . \tag{8}$$

B. Formalism for periodic quasi-one-dimensional polymers using the linear combination of atomic orbital expansion for the crystal orbitals

Assuming the z axis to be the polymer axis and that the constant electric field is applied in the same direction ($E_x=E_y=0$), the total Hamiltonian [Eq. (1)] reduces to

$$\hat{H}=\hat{H}_0-F_z z\ , \tag{1$'$}$$

with

$$F_z=eE_z\ . \tag{2$'$}$$

It has to be mentioned that nonzero electric-field components E_x and E_y perpendicular to the polymer axis do not cause any difficulty. Here they are assumed to be zero for the sake of clarity and simplicity of the equations.

The total operator $\hat{H}_F$ including the perturbation [Eq. (6)] (taking only the periodic part of the electric-field operator into account, which is responsible for the polarization effect) can now be written in the form

$$\hat{H}_F=\hat{H}_0=-ie^{ikz}eE_z(d/dk_z)e^{-ikz}\ , \tag{6$'$}$$

where k stands now for the nonzero wave-vector component k_z [$\mathbf{k}=(0,0,k_z)$]. In the *ab initio* Hartree-Fock crystal orbital method[13,14] as well as in most semiempirical approximations, the one-electron crystal orbitals $\varphi_n^{\mathbf{k}}(\mathbf{r})$ are expanded in a linear combination of atomic orbitals (LCAO):

$$\varphi_n^{\mathbf{k}}(\mathbf{r})=(2N+1)^{-1/2}e^{i\mathbf{k}\cdot\mathbf{r}}\sum_{j=-N}^{N}e^{ikja}\sum_{p=1}^{m}c_{np}^{k}\chi_p^{j}(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}\ . \tag{3$'$}$$

N stands for the number of neighboring cells whose interactions with the reference cell are taken explicitly into account (the strict neighbor approximation is used, which means that the same cutoff radius is used for all different types of integrals). $\chi_p^j(\mathbf{r})$ is a shorthand notation for the atomic orbital $\chi_p(\mathbf{r}-\mathbf{r}_j-\mathbf{r}_p)$ located in cell j at position $\mathbf{r}_p$, and m is the number of atomic orbitals in the elementary cell.

The Bloch function in the LCAO approximation defined in Eq. (3′) is now substituted into the Fock equation [Eq. (8)]. The operator eigenvalue equation is multiplied from the left with $\chi_q^0(\mathbf{r})$ and integrated over space coordinates. The further evaluation leads to the set of inhomogeneous systems of equations that has to be solved for the perturbed eigenvector coefficients c_{np}^k for each band n and each value of k:

$$\sum_p c_{np}^k \left[(F_{qp}^k - \varepsilon_n^k S_{qp}^k) + eE_z \sum_j ja\, e^{ikja} S_{qp}^{0j} - eE_z \sum_j e^{ikja} D_{qp}^{0j} \right] = ieE_z \sum_p (dc_{np}^k/dk) S_{qp}^k ,$$

$$q = 1,2,\ldots, \text{ up to the number of atomic orbitals} ,$$

$$n = 1,2,\ldots, \text{up to the number of bands} ,$$

$$k = 1,2,\ldots, \text{up to the number of } \mathbf{k} \text{ points} . \qquad (9)$$

F_{qp}^k and S_{qp}^k are the elements of the Fourier transforms of the Fock and overlap matrices in direct space, respectively:

$$F_{qp}^k = \sum_{j=-N}^{N} e^{ikja} F_{qp}^{0j} , \qquad (10a)$$

$$S_{qp}^k = \sum_{j=-N}^{N} e^{ikja} S_{qp}^{0j} . \qquad (10b)$$

In the first version of the corresponding computer program a twofold iterative procedure has been used to solve Eq. (9). In the first step the homogeneous system of equations had been solved. Afterwards, using the eigenvector coefficients $\{c_{np}^k\}$, the inhomogeneous part had been calculated. However, the inhomogeneous system of equations (9) can easily be transformed into a homogeneous system of equations by multiplying and dividing the terms of the sum on the right side by c_{np}^k. This leads to the final form of the system of equations as it is realized in the more-advanced computer program:

$$\sum_p c_{np}^k \left[(F_{qp}^k - \varepsilon_n^k S_{qp}^k) + eE_z \sum_j ja\, e^{ikja} S_{qp}^{0j} - eE_z \sum_j e^{ikja} D_{qp}^{0j} = ieE_z \sum_p (1/c_{np}^k)(dc_{np}^k/dk) S_{qp}^k \right] = 0 , \qquad (11)$$

where D_{qp}^{0j} is an element of the dipole matrix.

C. The iterative solution of the homogeneous system of equations

The individual steps of the iterative self-consistent-field procedure to calculate the electronic polarization due to the applied electric field on the periodic polymer are described in more details in the following paragraphs.

(i) The very first step is to solve the *ab initio* Hartree-Fock crystal orbital problem for the unperturbed periodic polymer:

$$\underline{F}^k \mathbf{c}_n^k = \varepsilon_n^k \underline{S}^k \mathbf{c}_n^k . \qquad (12)$$

The sets of the one-particle eigenvalues ε_n^k and the eigenvector coefficients $\{c_n^k\}$ are used as input data for the first iteration of Eq. (11). The dipole matrices $\underline{D}^{0j}$ $(j=-N,-N+1\ldots,N)$ are calculated first in the direct space and then Fourier transformed to matrices in k space. It is well known that the resulting Bloch orbitals are determined only with respect to an arbitrary phase factor, which poses a serious problem for the calculation of their derivatives with respect to k.

(ii) To solve the complete system of equations [Eq. (11)], which has to be performed for each band n and each k value separately, one needs the derivatives of the eigenvector coefficients $\{c_{np}^k\}$ with respect to k. These quantities are obtained in the following way.

For a given band n, and a given atomic orbital p, the set of complex coefficients $\{c_{np}^{k_i}\}$ for $k_i = 1,2,\ldots,$ up to the number of $\mathbf{k}$ points is fitted to a polynomial function in k. The real parts of the coefficients are an even function in k, and therefore the polynomial is of the form

$$c_{np}^{k(\text{real})} = a_1 + a_3 k^2 + a_5 k^4 + a_7 k^6 + \cdots . \qquad (13a)$$

The imaginary parts of the coefficients are an odd function of k and therefore they can be expanded in a polynomial of odd powers in k:

$$c_{np}^{k(\text{imag})} = b_1 + b_2 k + b_4 k^3 + b_6 k^5 + \cdots . \qquad (13b)$$

Different methods have been tested to obtain the optimal fit: (1) the real and imaginary parts of the coefficients are fitted in a polynomial expansion with the same maximal power in k; (2) the real and imaginary parts are fitted separately by a polynomial series with different maximal powers in k; (3) the real and the imaginary parts, respectively, are fitted in a Chebyshev polynomial. Of course, all three methods lead to the same final result for the derivatives dc_{np}^k/dk, but the computer time is less for (1) than for (2) and especially for (3). Once these polynomial functions have been obtained with the help of method (1) or (2), it is very easy to calculate the value of the derivative with respect to k for a given value k_i using Eqs. 13(a) and 13(b). In the case of method (3), one has to again use other appropriate programs to determine these quantities.

(iii) The complete homogeneous non-Hermitian system of equations [Eq. (11)] is built up for each band n and each value of k. The resulting eigenvectors have to be renormalized. The problems concerning the undetermined phase factor will be discussed later.

(iv) After having calculated the complete set of perturbed eigenvectors (for all bands and all k values), the charge-bond order matrices are computed. These $\underline{P}^{0j}$ matrices ($j=-N,-N+1,\ldots,N$) are in turn used to recalculate the Fock matrices $\underline{F}^{0j}$ and then the Fourier transforms $\underline{F}^{k}$. Then step (ii) (the polynomial fit of the complex coefficients) is repeated until the maximal difference between matrix elements of the charge-bond order matrix $\underline{P}^{00}$ for two successive cycles is less than a given threshold value. The number of iterations to achieve self-consistency is in the order of five to ten cycles for the simple model system poly(H_2).

D. Possible numerical and computational problems and their solutions

1. Band crossing

The first difficulty occurs in the *ab initio* Hartree-Fock energy-band-structure calculation of the unperturbed periodic polymer. To date there has been no general and simple way to decide without doubt whether energy bands are crossing each other or whether they avoid crossing due to local symmetry in the elementary cell or whether they cross at all. In the case of an elementary cell with only a few atoms, the calculation of the derivative of ε_n^k with respect to k and the inspection for a discontinuity may be helpful. In the case of more-complex chemical systems, where band crossing can be observed between many bands, this method will be very cumbersome. Another approach has been developed, namely to calculate the contribution of each eigenvector $\mathbf{c}_n^k$ to the number of electrons per band (in the closed-shell case each band is occupied by two electrons). This method turned out to be very promising; however, again for large elementary cells, it became too complicated. Therefore a program has been incorporated into the *ab initio* Hartree-Fock crystal orbital program that yields large-scale plots of the energy-band structure in the critical regions. By comparison with the coefficients of the different crystal orbitals, a unique decision could be made about the band crossing, and the eigenvectors could easily be reordered.

To avoid the manual work of reordering the Bloch orbitals, a useful concept has been developed and included in the computer program. The sequence of the energy bands at $k_i=0$ $(i=1)$ is taken as the reference state. Then the overlap integrals $S_{mn}^{k_i k_{i+1}}$ are calculated,

$$\int \varphi_m^{k_j}(\mathbf{r})\varphi_n^{k_{i+1}}(\mathbf{r})d\mathbf{r}\ , \tag{14}$$

between all Bloch functions at $k=k_i$ and $k=k_{i+1}$. The corresponding bands are detected by the maximal value of the overlap integral, which is in the order of 0.9, while the value is much smaller in those cases where the bands do not match. If it is necessary, the bands can now be easily reordered for the case where $k=k_{i+1}$. Then the sequence of the crystal orbitals at $k=k_{i+1}$ is used as the reference order, the overlap integrals $S^{k_{i+1}k_{i+2}}$ are computed, and the comparison is performed. The repetition of this procedure finally leads to a completely ordered energy-band structure. Furthermore, using the already calculated overlap matrix over atomic orbitals, the computation time is negligible, and the method is reliable even in the case of only a few k values in the Brillouin zone.

2. σ-π band separation

To transform the inhomogeneous system of equations [Eq. (9)] into a homogeneous one [Eq. (11)] it was necessary to divide the inhomogeneous term by the appropriate eigenvector coefficient. Though most organic polymers are π-electron systems, this would lead to numerical difficulties due to possible divisions by zero coefficients of the π atomic orbitals in the case of σ bands and vice versa. Therefore one has to treat the σ and π bands separately, which means that one has to identify the π bands and the number of π atomic orbitals (AO's). This is done automatically in the computer program in a way similar to the band crossing problem discussed earlier. The overlap integrals between states belonging to σ and π bands are exactly zero, and the π AO's can be detected by their nonzero coefficients in the corresponding states.

3. Phase factor of the Bloch function

It is well known that the one-electron Bloch functions obtained from the Hartree-Fock crystal orbital calculation are undetermined with respect to an arbitrary phase factor $e^{i\lambda}$. According to our experience based on numerous crystal orbital calculations of chemically different systems, only the phase factors $\lambda=0$ or $\lambda=\pi$ have been observed, which means that for a given band the sign of the coefficients for two successive k values may differ by a factor of -1 (the magnitude of the individual coefficients changes smoothly). It has to be mentioned that for the calculation of the charge-bond order matrices $\underline{P}^{0j}$, the problem of different phase factors is not relevant because one has to integrate over k. However, when the coefficients are to be fitted by a polynomial series in k this change in the phase factor would lead to serious difficulties. This problem is easily overcome by selecting the largest coefficient of each eigenvector at $k=0$ and assigning its sign to the coefficients of the corresponding eigenvector for all other k values by multiplying by the factor of $+1$ or -1, respectively, when its sign is the same or the opposite one. It has further been observed that the calculation of the eigenvectors of the non-Hermitian system of equations [Eq. (11)] with the help of an appropriate diagonalization routine from the IMSL (International Mathematics and Scientific Library) computer program library results in a phase factor common to all eigenvectors. This advantage has also been used in the actual calculations of the unperturbed and perturbed crystal orbitals.

E. Calculation of the electric polarizability and hyperpolarizability

Due to the polarization effect of the electric field, a dipole moment is induced in the system. The total dipole moment per elementary cell is then given by the expression

$$\boldsymbol{\mu}(\mathbf{E})=\boldsymbol{\mu}_0+\boldsymbol{\mu}^{\mathrm{ind}}(\mathbf{E}) \, , \tag{15}$$

where $\boldsymbol{\mu}_0$ is the permanent dipole moment of the unit cell in the absence of the electric field.

The induced dipole moment can also be expressed by the series expansion

$$\boldsymbol{\mu}^{\mathrm{ind}}(\mathbf{E})=\underline{\alpha}\mathbf{E}+\tfrac{1}{2}\underline{\beta}E^2+\tfrac{1}{6}\underline{\gamma}E^2\mathbf{E}+\cdots \, . \tag{16}$$

Here $\underline{\alpha}$ is the polarizability tensor and $\underline{\beta}$ and $\underline{\gamma}$ are the hyperpolarizability tensors. In the case of a constant electric field applied in the direction of the polymer axis, Eq. (16) simplifies to

$$\mu_z^{\mathrm{ind}}(E_z)=\alpha_{zz}E_z+\tfrac{1}{2}\beta_{zzz}E_z^2+\tfrac{1}{6}\gamma_{zzzz}E_z^3 \tag{17}$$

for the dominant elements of the tensors. The diagonal elements can also be obtained from the relations that result from the expansion of the dipole moment in E_z (Ref. 15) and the use of the Hellman-Feynman theorem:

$$\alpha_{zz}=\left|\frac{d\mu_z^{\mathrm{ind}}}{dE_z}\right|_{E_z=0} , \tag{18a}$$

$$\beta_{zzz}=\left|\frac{d^2\mu_z^{\mathrm{ind}}}{dE_z^2}\right|_{E_z=0} , \tag{18b}$$

$$\gamma_{zzzz}=\left|\frac{d^3\mu_z^{\mathrm{ind}}}{dE_z^3}\right|_{E_z=0} . \tag{18c}$$

In this work these quantities are calculated performing the following steps: (i) The polarized wave function will be computed as has been described in the preceding section in the presence of a constant electric field E_z. (ii) Using these polarized crystal orbitals, the total dipole moment $\mu_z(E_z)$ is evaluated according to the expression

$$\mu_z(E_z)=(a/\pi)\int dk \sum_{i=1}^{n^{\mathrm{occ}}}[\varphi_i(E_z)]^*|ez|\varphi_i^k(E_z)) \, . \tag{19}$$

The induced dipole moment $\mu_z^{\mathrm{ind}}(E_z)$ is then given by Eq. (15). In addition, the contribution of each band to $\mu_z^{\mathrm{ind}}(E_z)$ is calculated, allowing for a detailed analysis and interpretation, which finally may lead to specific proposals with respect to the chemical structure. The two steps (i) and (ii) are repeated for about six different field strengths E_{z_i} ranging from -0.003 to 0.003 a.u. (iii) The obtained series of induced dipole moments $\mu_z^{\mathrm{ind}}(E_{z_i})$ is then fitted to a polynomial expansion in E_z. It is then very easy to calculate the required derivatives with respect to E_z, which are given in Eqs. (18a)–(18c).

III. RESULTS AND DISCUSSION

The simple model system poly(H_2) has been chosen to investigate in detail the different numerical algorithms that have to be applied in the present method. Secondly, an extensive study on the same system is reported in the literature[5] so that the results of different methods can be compared with each other. The tables and figures in the following sections contain only the most important results.

As has been mentioned, the finite field method is a possible approach to determine the polarizability of poly(H_2), extrapolating the results from the cluster calculations to the infinite system. In this approach the induced dipole moment $\mu_z^{\mathrm{ind}}(E_z)$ is calculated as a function of E_z for the molecules $(H_2)_n$, with n ranging from 1 to 15. For large enough clusters the value of the polarizability per H_2 molecule will converge to an approximate limit of the polarizability of the infinite chain and can be compared with the result of the calculation of the energy-band structure in the presence of the electric field.

The geometry of poly(H_2) has been taken as in Ref. 5 with the H-H bond length of 2.0 a.u. and the translational lengths of 5.0, 8.0, and 10.0 a.u., respectively. The STO-3G basis set[16] has been employed for most of the calculations. Some results will be reported also using the minimal (MB), double-ζ (DZB), and double-ζ plus polarization (DZBP) basis sets by Clementi.[17]

A. poly(H_2): Effect of the number-of-neighbors interaction

We take 61 **k** points for the numerical integration over the Brillouin zone to calculate the charge-bond order matrices $\underline{P}^{0j}$ in direct space and to fit the complex LCAO coefficients of the Bloch functions in a power series of **k** up to 20 (to calculate the derivatives with respect to k). The effect of the number of neighbors taken into account is given in Table I for poly(H_2) with the repeating length of 5.0 a.u. On the average eight self-consistent-field (SCF) cycles were necessary to achieve a convergence of 10^{-6} for all elements of the $\underline{P}^{00}$ matrix. The results in Table I indicate that the value of the polarizability converges slowly with the number of interacting cells. All the following calculations were performed using the seventh-neighbor approximation in the strict sense (which means that for all types of integrals the same cutoff radii have been used).

TABLE I. The influence of the neighboring cells (n_c) on the polarizability of poly(H_2) using a repeat length of 5.0 a.u., 61 **k** points, and a power-series expansion of 20 terms for the coefficients.

n_c	α_{zz} (a.u.)	$\Delta\alpha_{zz}$ (a.u.)
1	12.468	0.0
2	12.900	0.432
3	13.038	0.138
4	13.090	0.052
5	13.117	0.027
6	13.133	0.016
7	13.143	0.010
10	13.162	0.019

TABLE II. The dependence of the polarizability of poly(H_2) on the number of **k** points (n_k) using the maximal power (n_p) of the expansion in k for the complex coefficients and for the real and imaginary parts (n_{pr} and n_{pi}) of the coefficients, respectively (repeat length 5.0 a.u.; number of interacting cells =7). In addition, the results are given for the expansion of coefficients using Chebyshev polynomials.

n_k	n_p	n_{pr}	n_{pi}	a_{zz} (n_p)	a_{zz} (n_{pr},n_{pi})	a_{zz} (Chebyshev)
11	10	10	9	12.632	12.621	13.122
21	20	20	19	13.087	13.095	13.127
31	30	30	29	13.092	13.087	13.127
41	40	40	39	13.083	13.083	13.127
51	50	50	49	13.090	13.087	13.127
61	60	60	59	13.422	13.189	13.135
91	90	90	89	13.782	13.609	13.127

B. poly(H_2): Comparison between different series expansions of the coefficients

It has been mentioned before that three different methods to fit the LCAO coefficients to a polynomial function of k have been tested. In the first two procedures the coefficients are adjusted to a simple power series in k with either equal or different lengths for the real and imaginary parts, respectively. The third method makes use of a Chebyshev polynomial, performed separately for the real and imaginary terms. In Table II the results are listed for poly(H_2) with the translational length of 5.0 a.u. and the seventh-neighbor interaction approximation. The number of k values that determine the maximal power of k in the expansion varies from 11 up to 91. It turns out that for this model system the Chebyshev polynomial is the most stable one and leads to the required accuracy already with relatively few **k** points (equivalent to the maximal power of the series in k). This is important because the necessary computation time is about five times higher than for the two other algorithms.

In addition, we have investigated the possibility of choosing different maximal powers in k for a given number of **k** points for the real and imaginary parts of the coefficients in the series expansion in k. In Table III the computational results are summarized using the Chebyshev polynomial and the power series in k, performed separately for the real and imaginary parts of the coefficients. It can be seen that the stability is less for the last method unless the maximal possible power of k is used. These preliminary investigations suggest that a large number of **k** points and in addition the therewith defined maximal power of k have to be applied for the polynomial fit in k. However, a significantly lower number of k values and a shorter polynomial series can be taken for the Chebyshev polynomial.

C. $(H_2)_n$ cluster: The polarizability per unit cell as a function of the cluster size

In Table IV we present the numerical results of the polarizability per H_2 molecule with increasing chain length

TABLE III. The dependence of the polarizability of poly(H_2) on the maximal powers (n_{pr},n_{pi}) of the series expansion for the real and imaginary parts of the coefficients, respectively, for different numbers of **k** points (n_k) (repeat length 5.0 a.u., number of neighboring cells =7).

		$n_k=61$		$n_k=91$
n_{pr}	n_{pi}	a_{zz} (Chebyshev)	a_{zz} (n_{pr},n_{pi})	a_{zz} (n_{pr},n_{pi})
19	19	13.273	13.087	13.139
19	20	13.273	13.133	13.143
20	19	13.273	13.143	13.149
29	29	13.127	13.092	13.132
29	30	13.127	13.110	13.119
30	29		13.111	13.124
39	39		13.083	13.383
39	40	13.127	13.096	13.105
40	39		13.096	13.380
49	49		13.090	13.104
49	50	13.127	13.096	13.105
50	49			13.103
59	59	13.135	13.075	13.256
59	60	13.135	13.982	13.632
60	59	13.135	13.189	13.950
60	60		13.823	

TABLE IV. The average polarizability per hydrogen molecule from $(H_2)_n$-cluster calculations for different repeat lengths using minimal and extended basis sets.

n	$\alpha_{zz}^{\text{STO-3G}}$	α_{zz}^{MB}	α_{zz}^{DZB}	$\alpha_{zz}^{\text{DZPB}}$	Repeat length
1	5.81	8.84	12.20	12.06	5.0
2	8.35				
3	9.92	15.04	18.34	18.40	
4	10.92				
5	11.58	17.86	21.44	21.56	
7	12.40	19.32	23.10	23.24	
9	12.88	20.20	24.10	24.26	
11	13.19	20.78	24.76	24.92	
13	13.14	21.18	25.08		
15	13.57	21.50	25.42		
1	5.81	8.84	12.20		8.0
3	6.05	9.42	13.08		
7	6.14	9.66	13.59		
9	6.15	9.70	13.66		
11	6.16	9.73	13.71		
1	5.81	8.84	12.20		10.0
3	5.91	8.98	12.68		
5	5.94	9.14	12.81		
7	5.95	9.17	12.87		
9	5.96	9.19	12.90		
11	5.97	9.20	12.92		

using the finite field approach. The numbers are given for minimal and extended basis sets (STO-3G, Clementi's MB, DZB, and DZBP). The calculations have been performed for three different intermolecular distances (5.0, 8.0, and 10.0 a.u.). In the case of the short intermolecular distance (3.0 a.u.), Clementi's minimal and double-ζ basis sets predict polarizabilities almost twice as large as for the STO-3G basis set. This fact is reflected also in the crystal orbital calculations, where for weakly alternating molecular hydrogen chains the extended basis set leads to numerical instabilities already at the Hartree-Fock level. This may be the reason that diffuse basis functions overestimate the polarizability in nearly equidistant chains of hydrogen atoms.

TABLE V. The polarizability per unit cell (H_2) as a function of the repeat length. A comparison between the finite-cluster approach $(H_2)_{15}$ and the crystal orbital method, using 31 **k** points, seven interacting cells, and 30 terms in the power-series expansion of the complex coefficients.

Repeat length	α_{zz} (crystal orbital)	α_{zz} (cluster)
5.0	13.13	13.56
5.5	10.57	9.53
6.0	8.99	7.81
7.0	7.26	6.54
8.0	6.49	6.16
9.0	6.16	6.03
10.0	6.01	5.97
12.0	5.91	5.90
100.0	5.81	5.81

The addition of a set of p-type polarization functions increases the α_{zz} value only about 1% compared with the DZB results. The table also shows that the polarizability of $(H_2)_n$ is strongly dependent on the intermolecular distance and that it converges slowly with increasing size of the cluster.

To verify our results we have repeated some of the cluster calculations with the help of the GAUSSIAN88 computer program using the STO-3G basis. The polarization tensor elements are computed on two different levels of approximation. The more sophisticated method leads to numbers that are identical to the results obtained in this work, while the approximate results agree with those reported in Ref. 5.

D. poly(H_2)-$(H_2)_n$: Comparison of the results for the polarizability obtained with the crystal orbital and the finite cluster approach

In Table V the results of the polarizability per unit cell are summarized as a function of the translation length using the STO-3G basis set. The calculations were performed for $(H_2)_{15}$ clusters and with the crystal orbital approach (seventh-neighbor interaction, Chebyshev polynomial expansion up to the 30th power for 31 **k** points), respectively. The results are graphically presented in Fig. 1 together with the corresponding results for Clementi's MB and DZB. It can be seen that the polarizability per elementary cell is a strongly dependent function on the translational length beginning at 7 a.u. Due to the end effects in the finite cluster calculations, the curves are

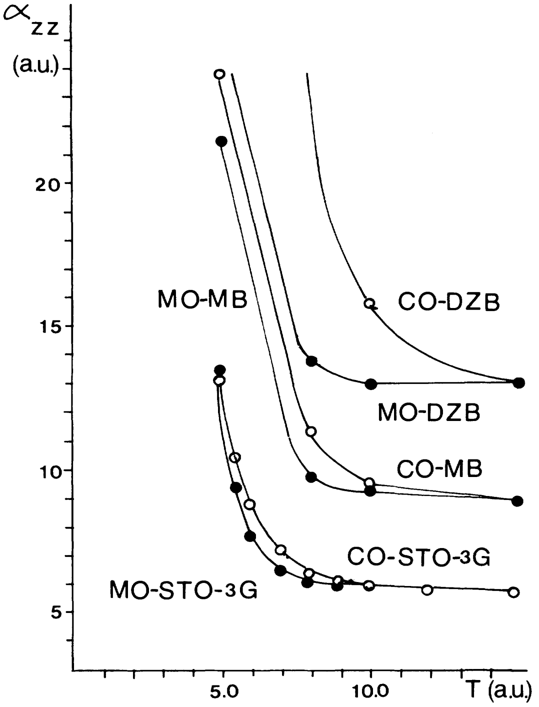

FIG. 1. The comparison of the polarizability α_{zz} per elementary cell using the finite field (MO) and crystal orbital (CO) methods, respectively, for different basis sets and translational lengths.

below the curves of the crystal orbital calculations for all employed basis sets. The computational results for the additionally investigated model systems, poly(H_2O) and poly(LiH), will not be reported in numerical details, but graphical representations will be given and discussed.

1. *Results for poly(H_2O)*

The water molecule is an example with a small polarizability. The relative geometrical arrangement of the molecules in the clusters and in the periodic polymer linked by hydrogen bonds is shown in Fig. 2(a). Clementi's minimal basis set has been used for the molecular and crystal orbital calculations. The polarizability per water molecule resulting from cluster calculations on $(H_2O)_n$ with $n = 1,2,\ldots,6$ is depicted in Fig. 2(a) for the intermolecular distance of 5.5 a.u. The convergence is slow, and the asymptotic value can be extrapolated to be about 6.5 a.u. for α_{zz}. This becomes understandable if one looks at the gross atomic population of the hydrogen atoms in the case of the cluster $(H_2O)_6$ [shown in Fig. 2(b)]. It is clearly seen that the end effects play an important role because the electronic charge of, e.g., H_1 in the six water molecules differs quite significantly. Figure 2(c) shows the comparison between the cluster approach for $(H_2O)_6$ and the new polymer concept for the polarizability using different intermolecular distances. Of course, for large repeating lengths both methods converge to the polarizability α_{zz} for an isolated water molecule.

2. *Results for poly(LiH)*

The Li-H bond length has been optimized for a trimer where the LiH sticks have been linearly arranged. The cluster and crystal orbital calculations have been performed using the STO-3G and Clementi's minimal basis, respectively. In Fig. 3(a) the results for the polarizability per unit of the calculations on $(LiH)_n$ clusters

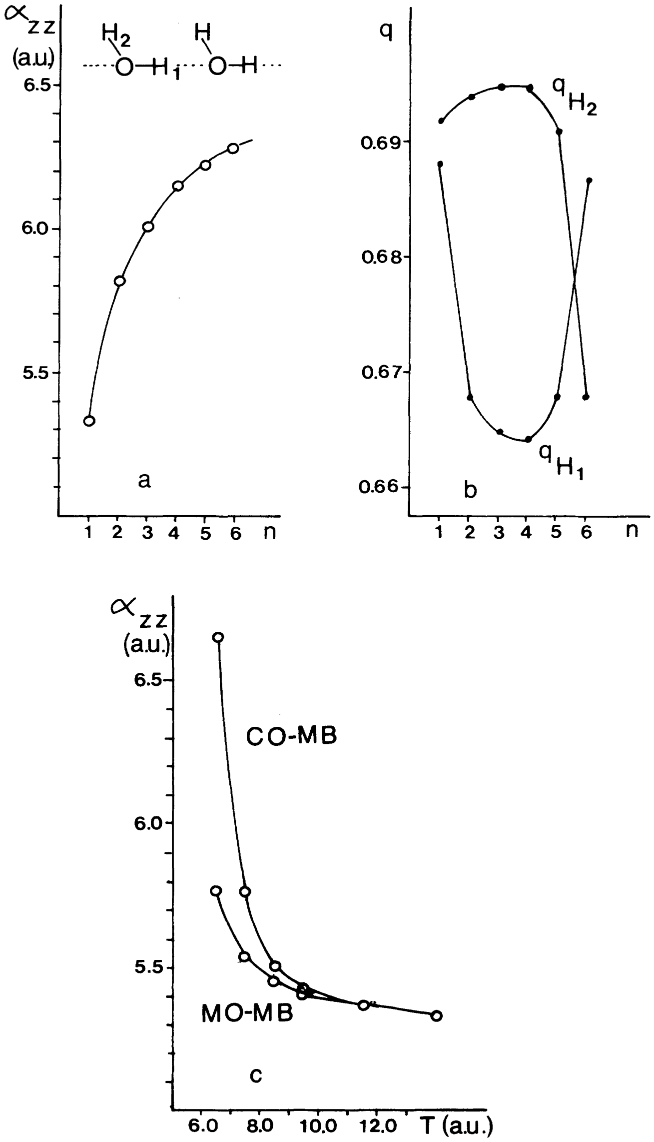

FIG. 2. (a) The polarizability α_{zz} per water molecule resulting from $(H_2O)_n$ cluster calculations ($n = 1,2,\ldots,6$). The repeating length is 5.5 a.u. (b) The gross atomic charge of the two H atoms in the $(H_2O)_6$ cluster. (c) The polarizability α_{zz} per elementary cell using the finite field (MO) and crystal orbital (CO) approaches, respectively, for different translational lengths.

($n = 1,2,\ldots,20$) are drawn for the intermolecular distance of 7.5 a.u. The use of Clementi's minimal basis set predicts a larger polarizability than for the STO-3G basis set. The additional points in Fig. 3(a) are obtained for $(LiH)_3$ and $(LiH)_4$ when one takes into account the potential of the infinite chain to the left and to the right of the finite cluster via a Madelung summation. In this way the end effect is partially corrected; and the rise is much steeper than without the inclusion of long-range interactions. The reason that the convergence is slow can be seen from Fig. 3(b), where the gross atomic charges of H and Li are drawn for the $(LiH)_{20}$ cluster with 7.5 a.u. intermolecular distance. The deviation of the electronic charge of the first three and the last three atoms is appreciable from one of the central atoms. Figure 3(c) again shows the comparison of the polarizability calculated with the help of the cluster ($n = 20$) and polymer approaches, respectively, as a function of the translational length. In both cases the minimal basis set by Clementi predicts higher polarizabilities than the STO-3G basis set. The reason is that the first one is more flexible, and, according to our numerous experiences in general, the results obtained with the help of this basis set are very close to the results obtained with a double-ζ basis set.

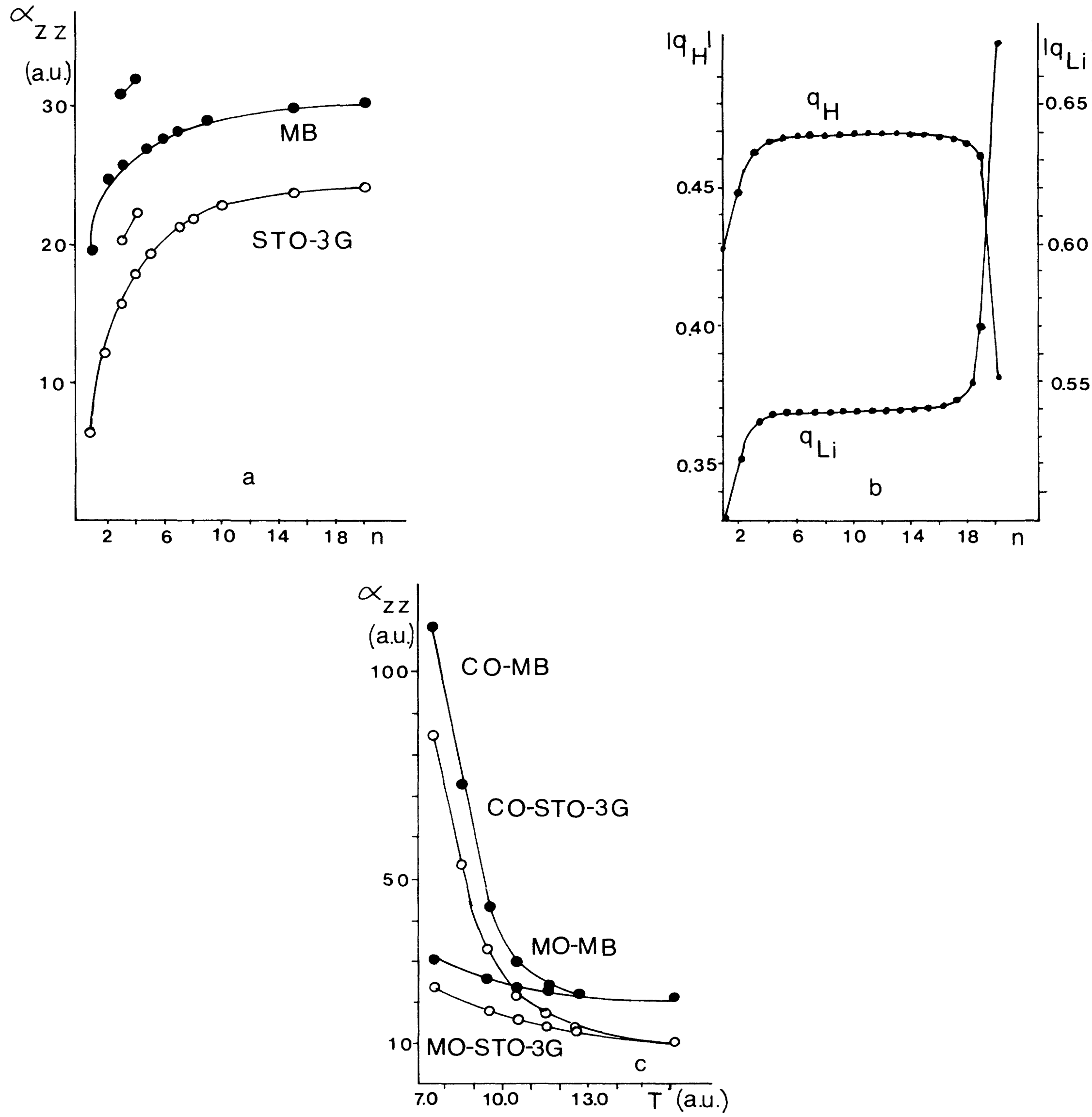

FIG. 3. (a) The polarizability α_{zz} per LiH molecule obtained from $(LiH)_n$ cluster calculations ($n = 1,2,\ldots,20$; the intermolecular distance is 7.5 a.u.) using the STO-3G and Clementi's minimal basis set, respectively. In addition, for $n = 3,4$ long-range interaction has been taken into account. (b) The absolute values of the net atomic charge for H and Li in the $(LiH)_{20}$ cluster. (c) The dependence of the polarizability per LiH unit on the repeating length calculated with the cluster and crystal orbital approaches, respectively.

IV. CONCLUSION

A theory has been developed and the numerical methods have been worked out to treat the effects of a constant homogeneous electric field on the energy-band structure of periodic polymers in a variational manner. The solution of the complex system of equations has to be performed in an iterative self-consistent-field approximation. The application of this method to calculate the induced dipole moment of a periodic chain as a function of the electric-field strength opens the possibility of obtaining the elements of the (hyper)polarizability tensor elements. The results obtained for the model systems poly(H_2), poly(H_2O), and poly(LiH) are quite stable with respect to various numerical techniques that have been tested in the course of the calculations. Further preliminary investigations on polyenes, which will be reported elsewhere, confirm these observations. In summary, this approach is a very promising one for the calculation of basic properties of polymers in the presence of an electric field.

ACKNOWLEDGMENTS

The author recognizes the help by Drs. W. Förner and O. Fleck for many interesting and stimulating discussions on the subject of this investigation. He also thanks Mr. A. Sutjianto for drawing attention to some relevant literature. The assistance by U. Salzner in performing the cluster calculations, using the GAUSSIAN88 program, is gratefully acknowledged.

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