

Calculation of Frequency-Dependent Polarizabilities of Quasi-One-Dimensional Systems

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Abstract

Calculations of frequency-dependent polarizabilities of quasi-one-dimensional systems are reported using the coupled Hartree-Fock method recently developed for polymers. Computations have been performed for infinite model chains of hydrogen and water molecules, respectively. The frequency dispersions applying different basis sets agree very well with theoretical results in the literature both for the chain and the respective molecule. In addition the dynamic polarizabilities of the conjugated periodic systems polyacetylene, polycarbonitrile and polyaziridine have been investigated.

Keywords: Frequency-dependent polarizabilities, quasi-one-dimensional systems, nonlinear optics, coupled Hartree-Fock method

Introduction

Nonlinear optics is a topic of intensive experimental research [1-4]. Recently, theoretical interest has increased rapidly in the investigation of nonlinear optical properties of molecules [5-10], polymers [11-13] and molecules of infinite chains [14,15]. The principal aims of the theoretical work in this field are not only to permit the developments required for electrooptical and all-optical signal processing, but also to predict and design new chemical compounds or polymers with better nonlinear optical properties.

In the case of molecules, a variety of methods has been developed to treat the interaction both with static as well as frequency dependent electric fields at different levels. The most commonly applied theories are based on the finite field approach using the uncoupled or coupled Hartree-Fock equations [16], and recently also the density functional meth-

ods [17]. In addition, perturbation theoretical methods, e.g. the sum over states approximation [18] have been derived. At present the theoretical developments in this topic go strongly into the direction to take electron correlation effects into account [7,19-21] with the help of Møller-Plesset perturbation theory. As it is well known correlation effects play a very important role to calculate reliable nonlinear optical properties for molecules. Until now the numerical treatment is restricted to small molecules, since another condition is the application of very large basis sets, especially when one is interested in hyperpolarizabilities.

The theoretical situation is much less advanced for polymers. In principle two approaches are possible to calculate the optical response properties per elementary cell, whereby the longitudinal polarization is more interesting than the polarizability perpendicular to the polymer chain. On one hand, clusters of increasing size can be investigated and the average values per unit can then be extrapolated to the infi-

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nite periodic system [14,15]. On the other hand, one can use quantum chemical methods for polymers implementing the uncoupled Hartree-Fock [22] and coupled Hartree-Fock [23] formalisms to compute polarizabilities per elementary cell of the periodic quasi-one-dimensional system. In these papers, however, the non-bounded nature of the $-e\vec{E}\vec{r}$ operator was not circumvented (see below). Numerous applications mainly on conjugated electron systems following the first line are reported by the group of Andre' e. In addition thorough investigations on model polymeric systems have been performed to determine the effect of chain conjugation, basis sets and electron correlation [2].

If one starts with ab initio Hartree-Fock band structure calculations [24], it is necessary to treat the above mentioned difficulty of the unbounded operator of the field which destroys the periodic symmetry of the polymer [25-27]. This is also true for the case of the interaction of a polymer with an electromagnetic field (laser light)[28]. The coupled Hartree-Fock equations have been derived for periodic systems to compute dynamic polarizabilities and hyperpolarizabilities, taking also into account correlation effects [11,12].

The fundamental problem to study a polymer in the presence of an electric external field, is that the periodicity of the polymer will be destroyed no matter how weak the field amplitude is [29], because the operator representing the potential of the electric field acting on the polymer is unbounded. Therefore, the Born-von Kármán cyclic boundary conditions cannot be applied and the field-dependent crystal orbitals and energy band structure cannot be determined. As a consequence, the uncoupled or coupled Hartree-Fock and finite field techniques cannot be applied straightforwardly to obtain the polarizabilities of infinite periodic systems. The alternative way is to treat the nonlinear optical properties of conjugated polymers with the help of a perturbation theoretical ansatz [16,30]. But its applications to systems with large elementary cells are formidable due to the very great computational requirements [31] and in the case of strong fields, the application of perturbation theory becomes questionable.

In order to obtain the asymptotic polarizabilities of infinite periodic systems, an approach has been proposed for the interaction with a homogeneous static electric field [26,27,32,33] where the unbounded external electric field potential operator has been split into two different parts. One part describes the polarization effect without destroying the periodicity of the polymer; the other part stands for the so-called polarization current and is responsible for the acceleration of the electrons (changing the momentum of the electrons). To calculate polarizabilities only the periodic part of the operator has to be taken into account. It has been applied to evaluate the static polarizabilities of model systems like infinite chains of hydrogen, water and lithium hydride molecules [26], and conjugated periodic systems with small unit cells, e.g. polyacetylene, polycyclopropene [27]. The results have shown that this method is superior to the cluster ap-

proach because even for such simple systems in the latter case the convergence of the extrapolation is very slow.

In this work, the previously proposed theoretical approach at the ab initio Hartree-Fock level [11] will be applied to compute the polarizabilities of polymers in the presence of a homogeneous frequency-dependent external electric field. Taking into account only the periodic part of the electric field potential operator, one can investigate the perturbed polymer, taking advantage of the translational periodicity of the systems. In the next section, the basic theory will be given with particular attention to the evaluation of the frequency-dependent polarizabilities.

Theory

The Coupled Hartree-Fock Equations

For the most general case we assume that we have a homogeneous electric field \vec{E} , which contains two parts, static and dynamic,

$$\vec{E} = \vec{E}_{st} + \sum_{m=1}^M \vec{E}_{\omega} \left(e^{im\omega t} + e^{-im\omega t} \right) = \vec{E}_{st} + \sum_{m=1}^M \vec{E}_{\omega} 2 \cos m\omega t \quad (1)$$

where \vec{E}_{st} is the static electric field and \vec{E}_{ω} is amplitude of the time-dependent electric field oscillating with frequency ω . Here we have taken into account also the overtones.

In this case, the total Hamiltonian of an n-electron system can be written as

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (2)$$

where \hat{H}_0 is the unperturbed Hamiltonian of the n-electron system, and \hat{H}' is the perturbation operator in the presence of the external electric field, which can be explicitly written as

$$\hat{H}' = -e\vec{E} \cdot \vec{r} = -e \left(\vec{E}_{st} + \sum_{m=1}^M \vec{E}_{\omega} \cos m\omega t \right) \cdot \vec{r} \quad (3)$$

Because $\vec{E} \cdot \vec{r}$ is unbounded and this destroys the translational symmetry of a periodic system, we have to treat first of all the problem of the unbounded operator $\vec{E} \cdot \vec{r}$.

It is easy to verify that for the gradient of the Bloch function $\varphi_n(\vec{k}, \vec{r})$

$$\varphi_n(\vec{k}, \vec{r}) = e^{i\vec{k}\cdot\vec{r}} U_n(\vec{k}, \vec{r}) \quad (4)$$

(here $U_n(\vec{k}, \vec{r})$ is lattice periodic) with respect to \vec{k}

$$\begin{aligned} \nabla_{\vec{k}} \varphi_n(\vec{k}, \vec{r}) &= i\vec{r} \varphi_n(\vec{k}, \vec{r}) + e^{i\vec{k}\cdot\vec{r}} \nabla_{\vec{k}} U_n(\vec{k}, \vec{r}) \\ &= i\vec{r} \varphi_n(\vec{k}, \vec{r}) + e^{i\vec{k}\cdot\vec{r}} \nabla_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} \varphi_n(\vec{k}, \vec{r}) \end{aligned} \quad (5)$$

After multiplying both sides of Eq(5) by $-ie\vec{E}$ and reordering the terms, one obtains the operator

$$\begin{aligned} -e\vec{E}\cdot\vec{r}\varphi_n(\vec{k}, \vec{r}) &= \\ -ie\vec{E}e^{i\vec{k}\cdot\vec{r}}\nabla_{\vec{k}}e^{-i\vec{k}\cdot\vec{r}}\varphi_n(\vec{k}, \vec{r}) &+ ie\vec{E}\cdot\nabla_{\vec{k}}\varphi_n(\vec{k}, \vec{r}) \end{aligned} \quad (6)$$

If we multiply Eq(6) from the left by a Bloch function belonging to band m with a value k' , we find for the matrix elements of the first term of Eq(6) on the right-hand side,

$$\begin{aligned} -ie\langle\varphi_m(\vec{k}', \vec{r})|\vec{E}e^{i\vec{k}\cdot\vec{r}}\nabla_{\vec{k}}e^{-i\vec{k}\cdot\vec{r}}|\varphi_n(\vec{k}, \vec{r})\rangle &= \\ -ie\vec{E}\int d\vec{r}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}U_m(\vec{k}', \vec{r})\nabla_{\vec{k}}U_n(\vec{k}, \vec{r}) & \end{aligned} \quad (7)$$

vanishes unless $\vec{k}' = \vec{k}$. This term describes the polarization of the system in the presence of \vec{E} . But it can be easily recognized that this part of the perturbation operator is nonhermitian. The second matrix element originating from the r.h.s. of Eq(6) is not lattice periodic. This term corresponds, however, to a polarization current because matrix elements with $\vec{k}' = \vec{k}$ do not vanish.

In the present study, we focus on the case of a monochromatic optical field without overtones that is $M = 1$ in the summation of Eq(1) and Eq(3), and have taken into account only the dynamic part of the external electric field ($\vec{E}_{st} = \vec{0}$). The perturbation operator \hat{H}' will be then

$$\hat{H}' = -ie\vec{E}_\omega e^{i\vec{k}\cdot\vec{r}}\nabla_{\vec{k}}e^{-i\vec{k}\cdot\vec{r}}\cos\omega t \quad (8)$$

One can substitute Eq(2) with (8) into Frenkel's variational principle which provides the condition for the existence of a stationary state

$$J = \frac{\langle\Phi|\hat{H}-i\frac{\partial}{\partial t}|\Phi\rangle}{\langle\Phi|\Phi\rangle} ; \quad \delta J = 0 \quad (9)$$

We apply for the time-dependent n-electron function the ansatz:

$$\begin{aligned} \Phi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{E}_\omega, \omega, t) &= \\ e^{-iW_0 t} \hat{A} \prod_{i=1}^n \tilde{\varphi}_i(\vec{r}_i, \vec{E}_\omega, \omega) t & \end{aligned} \quad (10)$$

where W_0 is the total energy of the n-electron system in the field-free case (the eigenvalue of \hat{H}_0). \hat{A} is the antisymmetrizer and the one-electron orbitals in the presence of the field are:

$$\begin{aligned} \tilde{\varphi}_i(\vec{r}_i, \vec{E}_\omega, \omega, t) &= \\ \varphi_i(\vec{r}_i) + \Delta\varphi_i^+(\vec{r}_i, \vec{E}_\omega) e^{i\omega t} &+ \Delta\varphi_i^-(\vec{r}_i, \vec{E}_\omega) e^{-i\omega t} \end{aligned} \quad (11)$$

here $\varphi_i(\vec{r}_i)$ is the eigenfunctions of Fock operator belonging to \hat{H}_0 .

To determine the effect of the time-dependent field $\vec{E}_\omega \cos\omega t$ one has to substitute Eq(10) with (11) into (9), and to perform the variation of J with respect to the unknown functions $\Delta\varphi_i^+$ and $\Delta\varphi_i^-$, respectively, under the orthogonality requirements [16]

$$\langle\varphi_i(\vec{r}_i)|\Delta\varphi_i^\pm(\vec{r}_i, \vec{E}_\omega)\rangle = 0 \quad (12)$$

$$\left[\langle\Delta\varphi_i^\pm(\vec{r}_i, \vec{E}_\omega)|\varphi_j(\vec{r}_j)\rangle + \langle\varphi_j(\vec{r}_j)|\Delta\varphi_i^\pm(\vec{r}_i, \vec{E}_\omega)\rangle \right] = 0$$

One obtains the coupled Hartree-Fock (RPA) equations for a closed shell system.

$$\begin{aligned} \left[\hat{F}_0 - \varepsilon_i^{(0)} \pm \omega \right] \Delta\varphi_i^\pm(\vec{r}_1, \vec{E}_\omega) &+ \hat{h}|\varphi_i(\vec{r}_1)\rangle \\ + \sum_{j=1}^{N/2} \left[\langle\varphi_j(\vec{r}_2)|\frac{2-\hat{P}_{1\leftrightarrow 2}}{r_{12}}|\Delta\varphi_j^\pm(\vec{r}_2, \vec{E}_\omega)\rangle_2 &+ h.c. \right] \\ |\varphi_j(\vec{r}_1)\rangle &= 0 \end{aligned} \quad (13)$$

$$(i = 1, 2, \dots, n)$$

here $\hat{h} = -ie\vec{E}_\omega e^{ik\vec{r}} \nabla_{\vec{r}} e^{-ik\vec{r}}$ and $\hat{P}_{1\leftrightarrow 2}$ is the permutation operator exchanging the coordinates of electron 1 with electron 2. Further in the case of a quasi-one-dimensional periodic polymer, the Fock operator of the unperturbed system is defined as

$$\hat{F}_0 = \sum_{j=1}^{N/2} \left\langle \Phi_j(\vec{r}_2) \left| \frac{2 - \hat{P}_{1\leftrightarrow 2}}{r_{12}} \right| \Phi_j(\vec{r}_2) \right\rangle + \hat{H}^N \quad (14)$$

$$\hat{H}^N = -\frac{1}{2} \nabla_1^2 - \sum_{l=1}^{2N+1} \sum_{\alpha=1}^{N_\alpha} \frac{Z_\alpha}{|\vec{r}_1 - \vec{R}_\alpha^l|}$$

where $(2N + 1)$ is the number of the unit cells in the polymer, N_α the number of nuclei in the unit cell, Z_α the charge of the α -th nucleus and, finally, \vec{R}_α^l is the position vector of the α -th nucleus in the l -th cell.

Formalism for periodic quasi-one-dimensional polymers in the LCAO approximation

For 1D periodic polymers, the one-electron crystal orbitals $\phi_i^k(\vec{r})$ are expanded in a linear combination of atomic orbitals (LCAO)

$$\phi_i^k(\vec{r}) = (2N + 1)^{-\frac{1}{2}} \sum_{l=-N}^N e^{ikla} \sum_{p=1}^{\tilde{m}} C_{ip}^k \chi_p^l(\vec{r}) \quad (15)$$

$$\Delta\phi_i^{\pm k}(\vec{r}, \vec{E}_\omega) = (2N + 1)^{-\frac{1}{2}} \sum_{l=-N}^N e^{ikla} \sum_{p=1}^{\tilde{m}} C_{ip}^{\pm k}(\vec{E}_\omega) \chi_p^l(\vec{r})$$

where N stands for the number of neighboring cells whose interactions with the reference cell are taken explicitly into account. $\chi_p^l(\vec{r})$ is a shorthand notation for the atomic orbital $\chi_p(\vec{r} - \vec{r}_l - \vec{r}_p)$ located in cell l at position \vec{r}_p , and \tilde{m} is the number of atomic orbitals in the elementary cell.

Substituting the LCAO ansatz of ϕ_i and $\Delta\phi_i^\pm$ into the coupled Hartree-Fock equations (Eq(13)), multiplying from the left with $\chi_q^0(\vec{r})$ and integrating over space coordinates, one obtains the following equations

$$\begin{aligned} & \sum_{l=-N}^N \sum_{p=1}^{\tilde{m}} C_{ip}^{\pm k}(\vec{E}_\omega) e^{ikla} \left[F_{qp}^{0,l} - (\epsilon_i^0 \pm \omega) \cdot S_{qp}^{0,l} \right] \\ & = \sum_{p=1}^{\tilde{m}} C_{ip}^k \left[\vec{E}_\omega \sum_{l=-N}^N e^{ikla} D_{qp}^{0,l} - |e| \vec{E}_\omega \sum_{l=-N}^N l a e^{ikla} S_{qp}^{0,l} - A_{qp}^\pm \right] \\ & + i |e| \vec{E}_\omega \sum_{l=-N}^N \sum_{p=1}^{\tilde{m}} \left(\frac{d}{dk_z} C_{ip}^k \right) \cdot e^{ikla} S_{qp}^{0,l} \end{aligned} \quad (16)$$

Here

$$\begin{aligned} A_{qp}^{k,\pm} & = \sum_{l_1=-N}^N \sum_{l_2=-N}^N \sum_{\mu=1}^{\tilde{m}} \sum_{\nu=1}^{\tilde{m}} \sum_{j=1}^{N/2} \left(2 \langle \chi_q^0 \chi_\mu^{l_1} | \chi_p^l \chi_\nu^{l_2} \rangle \right. \\ & \quad \left. - \langle \chi_q^0 \chi_\mu^{l_1} | \chi_\nu^{l_2} \chi_p^l \rangle \right) \times C_{j\mu}^{l_1,k} C_{j\nu}^{l_2,\pm k}(\vec{E}_\omega) \\ & + \sum_{l_1=-N}^N \sum_{l_2=-N}^N \sum_{\mu=1}^{\tilde{m}} \sum_{\nu=1}^{\tilde{m}} \sum_{j=1}^{N/2} \left(2 \langle \chi_q^0 \chi_\mu^{l_1} | \chi_p^l \chi_\nu^{l_2} \rangle \right. \\ & \quad \left. - \langle \chi_q^0 \chi_\mu^{l_1} | \chi_\nu^{l_2} \chi_p^l \rangle \right) \times C_{j\nu}^{l_1,\mp k}(\vec{E}_\omega) C_{j\mu}^{l_2,k} \end{aligned} \quad (17)$$

$D_{qp}^{0,l}$ is the matrix element of the dipole moment

$$D_{qp}^{0,l} = \langle \chi_q^0 | \vec{r} | \chi_p^l \rangle$$

and $S_{qp}^{0,l}$ is the overlap matrix element

$$S_{qp}^{0,l} = \langle \chi_q^0 | \chi_p^l \rangle$$

The above equations are linear algebraic equations in matrix form $\underline{AX} = \underline{B}$ [11].

Because of the nonhermicity of the operator \hat{h} (see Eq(7) and Eq(13)), we have to expand the crystal orbitals to the whole first Brillouin zone and to treat all matrices in the nonhermitian way.

Inspecting the system of equation (16) one should observe that because of the occurrence of the unknown $C_{ip}^{\pm k}$ in the r.h.s of Eq(16), these equations are non-linear and, therefore, have to be solved in an iterative way. But if we solve Eq(16) without taking into account the electron-electron interaction terms ($A_{qp}^{k,\pm}$ in Eq(16)), we reach the uncoupled Hartree-Fock equations.

After we solve the ab initio Hartree-Fock crystal orbital problem for the unperturbed periodic polymer. We use the

sets of the one-electron eigenvalues ($\epsilon_i^{0,k}$) and the eigenvector coefficients $\{C_{ip}^{0,k}\}$, as the initial values of $\{C_{ip}^{\pm k}(\vec{E}_\omega)\}$ for the first iteration of Eq(16).

After having solved the Eq(16) for all bands and all k values, the new one-electron wave functions (Eq(11)) should be renormalized with a normalization constant:

$$N_i = \left[\left\langle \varphi_i^k(\vec{r}) \middle| \varphi_i^k(\vec{r}) \right\rangle + \left\langle \Delta\varphi_i^{\pm k}(\vec{r}, \vec{E}_\omega) \middle| \Delta\varphi_i^{\pm k}(\vec{r}, \vec{E}_\omega) \right\rangle \right]^{-1/2} \quad (18)$$

Treatment of the phase factor and band crossing problems

From Eq(16) we know that we need the derivatives of the eigenvector coefficients $\{C_{ip}^k\}$ with respect to k . This can be done by expanding the real part of the eigenvector coefficients as a series of cosine functions and the imaginary part as a series of sine functions, respectively.

$$C_{ip}^{k(real)} = a_0 + a_1 \cos k + a_2 \cos 2k + \dots \quad (19)$$

$$C_{ip}^{k(imag)} = b_0 + b_1 \sin k + b_2 \sin 2k + \dots$$

Once one obtains the expansions for C_{ip}^k , it is easy to calculate the value of the derivatives with respect to k for a given value of k for each band.

In the case of band crossings and inconsistency of phase factors difficulties arise when we expand the eigenvector coefficients. Till now there is no general way to decide without doubt whether the energy bands are crossing each other or not. In order to reorder the bands, we apply the method one of us developed previously (see Ref. 26).

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,

$$\int \varphi_m^{k_i}(\vec{r}) \varphi_n^{k_{i+1}}(\vec{r}) d\vec{r} \quad (20)$$

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 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 $S_{i+1, k_{i+2}}$ 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.

Here it should be mentioned that without reordering of the crossing bands, there is no way to calculate the derivatives of C_{ip}^k .

The phase factors come from the one-electron Bloch functions obtained from the Hartree-Fock crystal orbital calculations with an undetermined arbitrary phase factor $e^{i\lambda}$. The most frequent cases in different systems are phase factors with $\lambda = 0, \pi$ or $\pi/2$, which means that for a given band the sign of the coefficients for two successive k values in our grid in k may be unchanged (the magnitude of the individual coefficients changes smoothly), i.e. $\lambda = 0$ case, or differ by a factor of -1 ($\lambda = \pi$ case) or exchange the values of real and imaginary parts of the coefficients ($\lambda = \pi/2$ case). These problems can be solved by inspecting the signs and the magnitudes of the coefficients. One way is to select the largest coefficient of each eigenvector coefficient at $k = 0$ point and assign its sign to all the coefficients belonging to other k values by multiplying with $+1$ or -1 , respectively, when their sign is the same or the opposite one. The other way is to minimize the imaginary part of the coefficients at the points $k = k_i$ ($i = 2, 3, \dots$) (at the point $k = k_1 = 0$ the imaginary part is zero). This can be achieved by determining the angle between the real axis and the complex vector and to perform afterwards the corresponding rotation. The angle for a given crystal orbital i is obtained from the relation

$$\tan \alpha = \frac{2 \sum_p C_{ip}^R \cdot C_{ip}^I}{\sum_p (C_{ip}^I)^2 - \sum_p (C_{ip}^R)^2} \quad (21)$$

where C_{ip}^R and C_{ip}^I are the real respective imaginary part of the coefficient C_{ip} . This procedure can be successfully used to solve the case if the phase factor $\lambda = \pi/2$. It should be mentioned that we use the combination of these two methods. For some complicated systems numerical difficulties still may exist for the eigenvector coefficients where one can observe a change of the phase factor within the first Brillouin zone.

Determination of SCF frequency-dependent polarizabilities

The most familiar definition[34] of polarizabilities is to expand the dipole moment in the presence of an external field \vec{E}

$$\begin{aligned} \mu^\lambda &= \langle \Phi(\bar{E}, t) | \hat{\mu}^\lambda | \Phi(\bar{E}, t) \rangle \\ &= \mu_0^\lambda + \sum_\mu \alpha^{\lambda\mu} E_\mu + \frac{1}{2!} \sum_{\mu,\nu} \beta^{\lambda\mu\nu} E_\mu E_\nu \\ &\quad + \frac{1}{3!} \sum_{\mu,\nu,\rho} \gamma^{\lambda\mu\nu\rho} E_\mu E_\nu E_\rho + \dots \end{aligned} \quad (22)$$

where λ, μ, ν, \dots represent x, y or z , μ_0 is the dipole moment in the absence of the field, $\underline{\alpha}$ is the linear polarizability, $\underline{\beta}$ is the first hyperpolarizability, and $\underline{\gamma}$ is the second hyperpolarizability tensor, respectively..

In case the external field \bar{E} is time-dependent with frequency ω

$$\bar{E} = E_\omega \cos \omega t \quad (23)$$

the induced dipole moment can be expanded as

$$\begin{aligned} \mu^\lambda &= \mu_0^\lambda + \sum_\mu \alpha^{\lambda\mu}(-\omega; \omega) E_{\omega,\mu} \cos \omega t \\ &\quad + \frac{1}{4} \sum_{\mu,\nu} \beta^{\lambda\mu\nu}(0; \omega, -\omega) E_{\omega,\mu} E_{\omega,\nu} \\ &\quad + \frac{1}{4} \sum_{\mu,\nu} \beta^{\lambda\mu\nu}(-2\omega; \omega, \omega) E_{\omega,\mu} E_{\omega,\nu} \cos 2\omega t + \dots \end{aligned} \quad (24)$$

After we solve the coupled Hartree-Fock equations (Eq(16)), we can expand the dipole moment as shown in Eq.(25) using the wave functions defined in Eq(11).

If we take the first derivatives of μ^λ with respect to $E_{\omega,\mu}$ at the point $\bar{E}_\omega = \bar{0}$, and compare the coefficients of the constant term and of $\cos \omega t$ term, respectively, we find that

$$\begin{aligned} &\langle \varphi_i^k + \Delta\varphi_i^{+,k} e^{i\omega t} + \Delta\varphi_i^{-,k} e^{-i\omega t} | \bar{r} | \varphi_i^k + \Delta\varphi_i^{+,k} e^{i\omega t} + \Delta\varphi_i^{-,k} e^{-i\omega t} \rangle \\ &= \left[\langle \varphi_i^k | \bar{r} | \varphi_i^k \rangle + \langle \Delta\varphi_i^{+,k} | \bar{r} | \Delta\varphi_i^{+,k} \rangle + \langle \Delta\varphi_i^{-,k} | \bar{r} | \Delta\varphi_i^{-,k} \rangle \right] + \left[\langle \varphi_i^k | \bar{r} | \varphi_i^{+,k} \rangle + \langle \Delta\varphi_i^{-,k} | \bar{r} | \varphi_i^k \rangle \right] e^{i\omega t} \\ &\quad + \left[\langle \varphi_i^k | \bar{r} | \varphi_i^{-,k} \rangle + \langle \Delta\varphi_i^{+,k} | \bar{r} | \varphi_i^k \rangle \right] e^{-i\omega t} + \left[\langle \Delta\varphi_i^{-,k} | \bar{r} | \Delta\varphi_i^{+,k} \rangle \right] e^{i2\omega t} + \left[\langle \Delta\varphi_i^{+,k} | \bar{r} | \Delta\varphi_i^{-,k} \rangle \right] e^{-i2\omega t} \\ &= \left[\langle \varphi_i^k | \bar{r} | \varphi_i^k \rangle + \langle \Delta\varphi_i^{+,k} | \bar{r} | \Delta\varphi_i^{+,k} \rangle + \langle \Delta\varphi_i^{-,k} | \bar{r} | \Delta\varphi_i^{-,k} \rangle \right] + \left[\langle \varphi_i^k | \bar{r} | \varphi_i^{+,k} \rangle + \langle \Delta\varphi_i^{-,k} | \bar{r} | \varphi_i^k \rangle \right] \cos \omega t \\ &\quad + \left[\langle \Delta\varphi_i^{-,k} | \bar{r} | \Delta\varphi_i^{+,k} \rangle \right] \cos 2\omega t \end{aligned} \quad (25)$$

$$\begin{aligned} \alpha^{\lambda\mu}(-\omega; \omega) &= \\ &= - \frac{\partial \left[\langle \varphi_i^k | \bar{r} | \Delta\varphi_i^{+,k} \rangle + \langle \Delta\varphi_i^{-,k} | \bar{r} | \varphi_i^k \rangle \right]}{\partial E_\omega^\mu} \Big|_{\bar{E}_\omega = \bar{0}} \end{aligned} \quad (26)$$

We choose 6 different electric fields strengths ranging from -0.002 to 0.002 a.u. in x, y, z directions and perform the numerical differentiation of Eq(26) to obtain $\alpha^{\lambda\mu}(-\omega; \omega)$.

Results and Discussion

The newly developed program for the calculation of dynamic polarizabilities has been added to our polymer program [35] (requests for the source code should be addressed to the authors). The calculations have been performed on a CRAY/Y-MP. Except for the calculation of the energy band structure the new programs are under development and not fully optimized with respect to vectorization. Furthermore, extrapolation procedures had not been activated for the presented calculations, therefore we think it will not be very informative to give more technical details. Optimization of the program is in work.

Molecular Hydrogen Chain

The frequency-dependent polarizability of the hydrogen chain has been evaluated at the coupled Hartree-Fock level. For the reason of comparison the uncoupled results are presented as well. For the geometry of the hydrogen chain the intramolecular distance at 2.0 a.u. and the intermolecular distance 5.0 a.u. respectively, has been taken. The results obtained for the hydrogen chain using Clementi's minimal basis set (MB) and double-zeta basis set (DZ) are presented in Figure 1. In the present work, we take 21 k points in the half first Brillouin zone for the numerical integration to calculate the charge-bond order matrices and to fit the unperturbed eigenvector coefficients in a power series of cosine and sine functions for their real and imaginary parts respectively.

From Figure 1, we find that the coupled Hartree-Fock polarizability of the hydrogen chain for MB and DZ are all

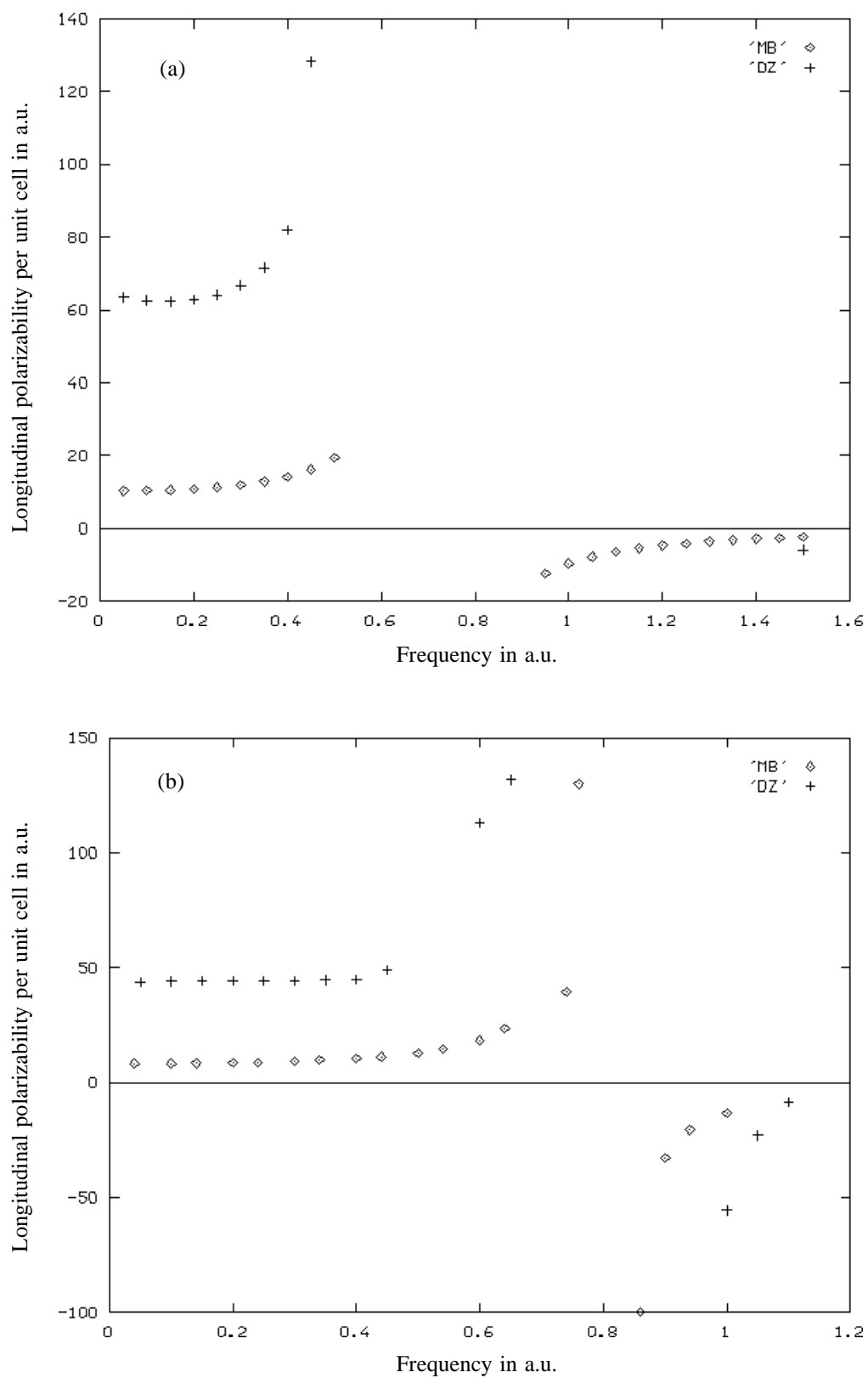


Figure 1. (a) coupled and (b) uncoupled frequency-dispersion curves of the longitudinal polarizability of the hydrogen chain for MB and DZ basis sets.

Table 1. Components of the polarizability (a.u.) of hydrogen molecule for different basis sets at the frequency $\omega = 0.0656$ a.u.

Basis Sets	$\alpha^{xx} = \alpha^{yy}$	α^{zz}	$\bar{\alpha}$ [a]	$\Delta\alpha$ [b]
MB	0.0	5.155	1.718	5.155
DZ	0.0	6.073	2.024	6.073
DZ+P	0.699	6.074	2.491	4.740
3s2p [c]	4.420	6.661	5.150	2.191
3s2p [d]	4.3940	6.5481	5.112	2.154
Exp.			5.43 [e]	2.035 [f]

$$[a] \bar{\alpha} = (\alpha^{xx} + \alpha^{yy} + \alpha^{zz})/3$$

$$[b] \Delta\alpha = 1/\sqrt{2} [(\alpha^{xx} - \alpha^{yy})^2 + (\alpha^{xx} - \alpha^{zz})^2 + (\alpha^{yy} - \alpha^{zz})^2]^{1/2}$$

[c] Basis set taken from: Sadlej, A. J. *Coll. Czech. Chem. Commun.* **1988**, 53, 1995; Sadley, A. *Theoret. Chim. Acta.* **1991**, 79, 123.

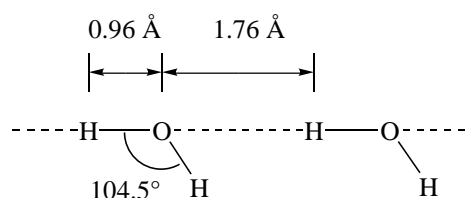
[d] Results with the same basis set as 3s2p [c] from Sekino and Bartlett, see Table 4 of Ref. 9.

[e] Newell, A. C. and Baird, R. C. *J. Appl. Phys.* **1965**, 36, 3751.

[f] MacAdam, K. B. and Ramsay, N. F. *Phys. Rev.* **1972**, A6, 898.

larger than the uncoupled ones. This is due to the inclusion of the electron-electron interactions in the coupled Hartree-Fock scheme. The positions of the first excitation energies resulting from the uncoupled Hartree-Fock calculations are all shifted to larger values in the coupled case. The numerical results and the dispersion of the longitudinal polarizability per unit cell of the hydrogen chain is in very good agreement with the results reported in Ref. 13.

For the reason of comparison with the polarizability of a hydrogen molecule, in Table 1 we summarize the results of Ref. 10 and the present work with the same geometry as in Ref. 10 and taking the translational vector infinite (10^7 a.u.). From Table 1, we see that the basis sets play an important role in the calculations of polarizabilities. Only with very large basis sets, can the numbers be compared with the ex-

**Figure 2.** Geometry of the water chain.**Table 2.** Components of the polarizability (a.u.) of the water chain [a].

Frequency	α^{xx}	α^{yy}	α^{zz}	$\bar{\alpha}$
MB				
0.0652	5.6866	0.4975	9.2279	5.1373
	4.9194	0.3929	9.0844	4.7989
0.0654	5.6868	0.5361	8.9520	5.0583
	4.9195	0.4496	9.0943	4.8211
0.0656	5.6870	0.4061	9.2431	5.1122
	4.9196	0.3106	9.1042	4.7781
0.0658	5.6871	0.3224	9.2507	5.0867
	4.9197	0.2391	9.1142	4.7577
0.0660	5.6873	0.2889	9.2584	5.0782
	4.9198	0.2167	9.1242	4.7536
DZ				
0.0652	13.4398	8.7717	42.2004	21.4706
	12.7222	7.7868	37.6132	19.3740
0.0654	13.4404	8.7297	42.2076	21.4592
	12.7226	7.6465	37.6220	19.3303
0.0656	13.4409	8.7332	42.2147	21.4629
	12.7230	7.6769	37.6308	19.3436
0.0658	13.4415	8.7781	42.2219	21.4805
	12.7233	7.8203	37.6397	19.3944
0.0660	13.4420	8.8390	42.2291	21.5034
	12.7237	7.9105	37.6486	19.4276
DZ+P				
0.0652	13.3734	9.2996	42.4149	21.6960
	13.3200	9.0657	38.8739	20.4199
0.0654	13.3739	9.4090	42.4241	21.7357
	13.3203	9.1190	38.8851	20.4415
0.0656	13.3744	9.5014	42.4332	21.7697
	13.3207	9.1475	38.8963	20.4548
0.0658	13.3749	9.5764	42.4425	21.7979
	13.3211	9.1642	38.9075	20.4643
0.0660	13.3754	9.6360	42.4518	21.8211
	13.3214	9.1748	38.9189	20.4717

[a] $\bar{\alpha} = (\alpha^{xx} + \alpha^{yy} + \alpha^{zz})/3$, geometry see Figure 2.

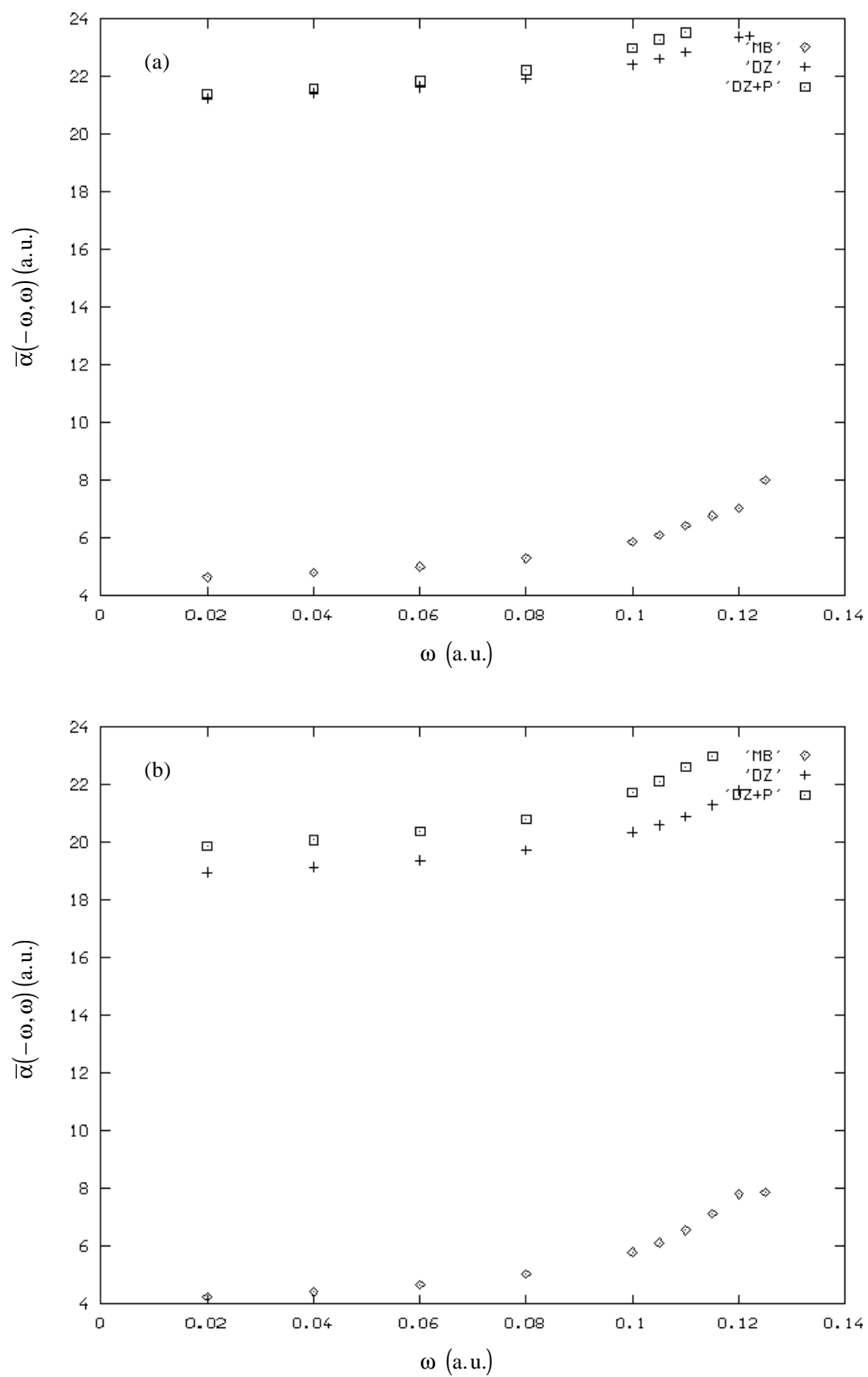


Figure 3. (a) coupled and (b) uncoupled frequency-dependent polarizability of the water chain for MB, DZ and DZ+P basis sets.

perimental ones. The similar results of Ref. 10 and of this work which we obtained using a larger basis set and performing the limiting procedure from polymer to molecule, proves the reliability of this approach. This stimulates us to apply larger basis sets (include polarization functions).

Water Chain

The model geometry we take in the calculations of the water chain is shown in Figure 2. The translational vector is 2.72 Å, in this hydrogen-bonded system.

In Figure 3, we show the time-dependent coupled and uncoupled Hartree-Fock calculations of the frequency-dependent polarizability for Clementi's MB, DZ and double-zeta with polarization functions (DZ+P)(p function on hydrogen has exponent 1.0; d function on oxygen has exponent 1.154). In Table 2, we summarize the results of the individual components of the frequency-dependent polarizability for Clementi's MB, DZ and DZ+P at the frequencies ranging from 0.0652 a.u. to 0.0660 a.u.

It is known that the basis set for the polarizability calculations should be adequate. The prediction of the polarizabilities depends upon products of matrix elements of the electron position operator \vec{r} . Consequently, in the study of polarizabilities one should take basis sets with an adequate description of the more diffuse regions of the crystal orbitals. From Figure 3 one can find that the basis set dependence is evident. Clementi's DZ and DZ+P basis sets yield more reliable values than the MB basis set. The polarizability for MB are always lower than the results for DZ and DZ+P, but the results for DZ and DZ+P are very similar. Therefore, in the following discussion, we only present the results of DZ or DZ+P basis sets.

From Table 2, and Figure 3 as well, we find that by introducing the polarization functions into the DZ basis set, the polarizability increases only to a small extent. For example, at the frequency 0.0656 a.u., $\bar{\alpha}$ for DZ is 21.4629 a.u., while for DZ+P is 21.7697 a.u. The difference is about 0.3 a.u.

In Figure 3 and Table 2, we also report the uncoupled results. Due to the inclusion of the electron-electron interactions in the coupled Hartree-Fock calculations, the coupled results are larger than the uncoupled ones. In Table 2, the first line of each frequency is the coupled Hartree-Fock results and the second line gives the uncoupled Hartree-Fock ones. The coupled results are always 5 to 10 percent larger than the uncoupled ones.

The geometry of the water chain we have chosen is the hydrogen-bonded structure. The hydrogen bond is along the polymer direction (Figure 2). It is not surprising that along the polymer axis (taken as the z-axis), the polarizability should be larger than that in the other directions. In Table 2, the α^{zz} component with different basis sets are much larger than the other components α^{xx} and α^{yy} , as it is to be expected.

To compare our results with the polarizability of a water molecule reported in Ref. 10, we take the same geometry as

Table 3. Components of the polarizability (a.u.) of polyacetylene (PA), polycarbonitrile (PC) and polyaziridine (PZ) using Clementi's DZ basis set at the frequency $\omega = 0.0656$ a.u. [a].

	α^{xx}	α^{yy}	α^{zz}	$\bar{\alpha}$
PA	43.2882	43.1108	266.2179	117.5390
PC	12.1473	15.6583	210.9440	79.5832
PZ	34.0674	47.4683	431.3693	170.9683

$$[a] \bar{\alpha} = (\alpha^{xx} + \alpha^{yy} + \alpha^{zz})/3.$$

in Ref. 10 and the same basis set level [5s3p2d/3s2p] and perform the limiting procedure from polymer to molecule as we did for hydrogen molecule. Our results are encouraging when we compare with the results in Table XI in Ref. 10. All the components (α^{xx} : 6.254, α^{yy} : 7.864, α^{zz} : 7.297) are in good agreement with the results of Ref. 10 (α^{xx} : 7.8428, α^{yy} : 9.1647, α^{zz} : 8.4993).

Polyacetylene(PA), polycarbonitrile(PC) and polyaziridine (PZ)

In Table 3, we report the frequency-dependent polarizabilities of poly(-CH=CH-)(PA), poly(-CH=N)(PC) and poly($\begin{smallmatrix} \text{NH} \\ \text{---} \\ \text{---} \end{smallmatrix}$)(PZ) evaluated at the coupled Hartree-Fock level at the frequency $\omega = 0.0656$ a.u. using Clementi's DZ basis set. Comparing with the results listed in Table 2 and Table 3, we can see that the polarizability for these conjugated π -electron systems are larger than those of water and hydrogen model chains. One can compare the frequency-dependent longitudinal polarizability of PA $\alpha^{zz} = 266.2$ a.u. (DZ basis set) to the static longitudinal polarizability $\alpha^{zz} = 150.1$ a.u. (3-21G) reported in Ref. 18. This shows that the dispersion is reasonable at this basis set level. However, it has to be mentioned that the calculations were not performed on the highest level with respect to the basis set and that the polarizabilities should not be compared with the experimental values.

Conclusions and Perspectives

Ab initio frequency-dependent polarizabilities of quasi-one-dimensional systems have been calculated at the time-dependent coupled Hartree-Fock level by using the random phase approximation (RPA). The basis set dependence and the frequency dispersion were discussed and the results were compared with results available in the literatures. The conclusions can be drawn that the new approach leads to reliable

results and is superior to the cluster method because in the latter case even for simple systems the convergence of the extrapolation is very slow.

However, to obtain the solutions of Eq(16), one has to inspect very carefully the phase factors and band crossings. This will be much more complicated for larger unit cells or larger basis sets. Moreover, to obtain the frequency-dispersion curves, one needs to solve Eq(16) for each frequency of interest. The more one reaches the excitation energy, the more difficult it is to obtain convergence. In addition, to obtain the hyperpolarizabilities, one needs to expand the one-electron orbital ansatz [11] to higher orders, and therefore the coupled Hartree-Fock equations will become more complicated. The development of the program of the evaluation of hyperpolarizabilities based on this extension is in progress in our Group.

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