Eur. Phys. J. B **17**, 623–627 (2000)

THE EUROPEAN
PHYSICAL JOURNAL B
EDP Sciences

Dielectric response of cylindrical nanostructures in a magnetic field[⋆]

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Received 11 January 2000 and Received in final form 19 May 2000

Abstract. We study the magnetic field dependence of the dielectric response of large cylindrical molecules such as nanotubes. When a field-induced level crossing takes place, an applied electric field has two effects: it may cause a linear instead of the usual quadratic Stark effect or the difference in the quadratic Stark coefficient of the two levels leads to a discontinuity in the polarization. Explicit calculations are performed for doped nanotubes and a rich structure in the real part of the low-frequency dielectric function $\epsilon'(H)$ is found when a magnetic field is applied along the cylinder axis. It is suggested that studies of $\epsilon'(H, T)$ can serve as a spectroscopic tool for the investigation of large ring-shaped or cylindrical molecules.

PACS. 77.22.-d Dielectric properties of solids and liquids – 78.40.Ri Fullerenes and related materials – 75.20.-g Diamagnetism and paramagnetism – 73.23.-b Mesoscopic systems

1 Introduction

During the last years considerable progress has been made in precise measurements of the real part of the low-frequency dielectric function $\epsilon'(\omega)$. In particular those measurements could be extended to ultra-low temperatures, *i.e.*, down to a few mK. Ratios of $\delta\epsilon'/\epsilon'$ up to 10^{-7} were achieved in that temperature regime. A rather spectacular success associated with that progress was the observation of a strong magnetic-field dependence of the polarizability of multicomponent glasses in the mK regime [1,2]. This development suggests reconsideration of magnetic field effects on ring molecules or related structures like nanotubes. That a magnetic field can have a considerable effect on the polarizability of an electron system was pointed out in [9–11] where small metallic particles of various shapes, *e.g.*, spheres, disks and rings were studied in connection with weak localization phenomena. We want to point out here that the magnetic field effect is particularly large when large ring molecules or nanotubes are considered. In both cases an applied magnetic field induces a diamagnetic ring current. Due to this current the energy of the ground state increases quadratically with the applied magnetic field. This continues until one of the excited states which lowers its energy in a field crosses the ground-state and becomes the new ground state. At the crossing point an applied electric field may cause a linear Stark effect, instead of the usual quadratic one and hence a divergent electric polarizability may result. This assumes a finite matrix element of the perturbation between the two crossing levels. But even when this matrix element is zero, a difference in the coefficient of the quadratic Stark effect for the two levels leads to a discontinuity in the dielectric response. The physical origin of the crossover is easily understood. An excited state carrying a ring current in the absence of a magnetic field becomes a state without a ring current, when a sufficiently high magnetic field is applied, because the induced current may cancel the original one. When this is the case the energy of that state equals the one of the ground state in the absence of a field. This simple argument shows that the ground-state energy is a periodic function of an applied magnetic field. The periodicity is given by the flux enclosed by the ring current. When one flux quantum $\phi_0 = hc/e$ is penetrating the ring the ground-state energy has returned to its original value. It is well known that a huge field of order 10^5 T is needed for a flux quantum ϕ_0 to penetrate a benzene molecule consisting of a ring of six carbon atoms. Because of that large value of the magnetic field, effects of it on ring molecules have obtained only little attention in the past [3,4]. The purpose of the present paper is to point out that the situation has changed considerably. Not only has there been experimental progress in performing high precision measurements of ϵ' at low temperatures, but also the synthesis of organic structures has made impressive advances. For example, nanotubes of large circumference have been produced, lowering the field required for the enclosure of a flux unit. In this paper we want to demonstrate that a measurement of $\epsilon'(H, T)$ should provide important information on the electronic excitations of ring molecules, in particular on level crossings. As a first step, we calculate here the dielectric response of a molecule consisting

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[⋆] Dedicated to K. Biedenkopf on the occasion of his 70th birthday.

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of a square lattice, *e.g.*, of carbon sites bent into a cylindrical form and of a nanotube, *i.e.*, a bent honeycomb lattice. Various extensions of the work presented here will follow later.

The magnetic and electric field are assumed to be directed along the cylindrical axis. The electron interactions are assumed to be included in effective one-electron parameters like in an extended Hückel theory or in the quasiparticle theory of Landau. In a subsequent investigation we shall include the electronic interactions more explicitly than done here. This may have profound effects on the results. A rich structure in $\epsilon'(H,T)$ is obtained which should be experimentally observable. It is closely related to the low-energy excitations of the systems in an applied magnetic field and in particular to level crossings as the field changes. Although our findings are limited here to the cylindrical structures described above, they suggest detailed experimental studies of $\epsilon'(H,T)$ for ring molecules.

In order to explain the main features of $\epsilon'(H,T)$ we consider first a single ring of N sites in a magnetic field along the ring axis. The Hamiltonian is

$$H = t \sum_{n,\sigma}^{N-1} (a^{+}_{(n+1)\sigma}\, a_{n\sigma}\, \mathrm{e}^{\frac{2\pi \mathrm{i}\phi}{N}} + \mathrm{h.c.}) \tag{1}$$

where $a^{+}_{n\sigma}, a_{n\sigma}$ are electron creation and annihilation operators and ϕ is the magnetic flux through the ring in units of the flux quantum ϕ_0. The resulting energy eigenvalues are

$$\epsilon(q) = 2t\,\cos\left[\frac{2\pi}{N}(q+\phi)\right], \qquad q = 0, \pm 1, \pm 2, ... \tag{2}$$

The ground-state energy E_g is periodic in the flux, *i.e.*, $E_\mathrm{g}(\phi+1) = E_\mathrm{g}(\phi)$. More explicitly when $\phi \le \frac{1}{2}$ we write for E_g

$$\begin{aligned} E_\mathrm{g}(\phi) = \sum_{\mathrm{occ}} 2t\,&\left[\cos\left(\frac{2\pi}{N}q\right)\,\cos\left(\frac{2\pi}{N}\phi\right)\right.\\ &\left. -\sin\left(\frac{2\pi}{N}q\right)\,\sin\left(\frac{2\pi}{N}\phi\right)\right]. \end{aligned} \tag{3}$$

For a closed-shell system, *i.e.*, for an electron number $N_e = 4n+2$, where n is an integer we find that

$$\sum_{\mathrm{occ}} \sin\frac{2\pi}{N} q = 0. \tag{4}$$

In that case the field-dependent contribution to the ground-state energy is

$$\begin{aligned} \delta E_\mathrm{g}(\phi) &= \sum_{\mathrm{occ}} 2t\,\cos\left(\frac{2\pi}{N}q\right)\left(\cos\left(\frac{2\pi}{N}\phi\right) - 1\right)\\ &= -E_\mathrm{g}(0)\left(1 - \cos\left(\frac{2\pi}{N}\phi\right)\right). \end{aligned} \tag{5}$$

For large N we may expand this expression and obtain

$$\delta E_\mathrm{g}(\phi) = -E_\mathrm{g}(0)\,\frac{2\pi^2}{N^2}\,\phi^2 > 0 \tag{6}$$

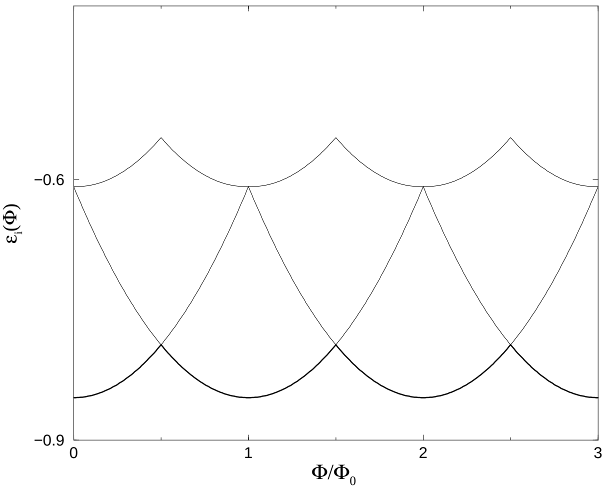

Fig. 1. Lowest three eigenvalues ϵ_i (*i.e.*, ground-state energy and first and second excited state) for a ring of N_e electrons (see text) as function of flux ϕ through the ring (in arbitrary units). The energy ratio of the second excited state and the ground state is independent of flux.

for $\phi \le \frac{1}{2}$. When $\phi = \frac{1}{2}$ the ground state is twofold degenerate because of a level crossing at that point. For $\phi > \frac{1}{2}$, the expression (3) is replaced by

$$\delta E_\mathrm{g}(\phi) = -E_\mathrm{g}(0)\,\frac{2\pi^2}{N^2}\,(1-\phi)^2, \qquad \frac{3}{2} > \phi > \frac{1}{2}\cdot \tag{7}$$

The behaviour of $\delta E_\mathrm{g}(\phi)$ is schematically shown in Figure 1. The contribution of $\delta E_\mathrm{g}(\phi)$ to $E_\mathrm{g}(\phi)$ is very small for large values of N and hardly detectable. This does not hold true though for other quantities. For example, when in addition an electric field is applied perpendicularly to the ring axis its effect on the ground-state energy is strongly dependent on ϕ. For $\phi = \frac{1}{2}$ we are dealing with a linear Stark effect instead of a quadratic one when $\phi \ne \frac{1}{2}$. Therefore the dielectric constant has a singularity at that particular value of ϕ. This simple example sheds light onto the physical reason why the dielectric function can be so sensitive to an applied magnetic field. The same feature is found for cylindrical molecules which are subject of this paper.

2 Magnetic-field dependence of the free energy

In order to demonstrate the influence of an applied magnetic field **H** on the free energy we consider two different systems. One is a model square lattice rolled into the form of a cylinder. The other one is a nanotube which consists of a honeycomb lattice rolled into a cylinder in the same way.

We start with the square lattice forming a cylinder. It consists of N atoms along the perimeter and of M atoms along the cylindrical axis z. The eigenvalues depend on the flux ϕ through the cylinder and are of the form

$$\epsilon_{pq\sigma} = -\cos\left[\frac{2\pi}{N}\,(p+\phi)\right] - t\cos\left[\frac{2\pi}{M+1}\,q\right] + 2\pi^2\,\frac{m_{\rm eff}\sigma}{m}\,\frac{\phi}{N^2}\cdot \quad (8)$$

The first term corresponds to a transfer integral of size $-\frac{1}{2}$ along the perimeter and the second to one of magnitude $-\frac{t}{2}$ along the z-axis. The parameters p and q take the integer values $p = 1, ..., N$ and $q = 1, ..., M$, respectively. The last term is the Zeeman contribution which is expressed here in terms of the flux ϕ. Since the latter is in units of the flux quantum ϕ_0, the ratio of the effective mass $m_{\rm eff}$ divided by the electron mass m enters here, with the former referring to an electronic motion perpendicular to the z-axis. Furthermore, $\sigma = \pm 1$. The free energy of the system is of the usual form

$$\beta F = -\sum_{pq\sigma} \ln[1+\exp(-\beta(\epsilon_{pq\sigma}-\mu))] \quad (9)$$

where $\beta = (k_{\rm B}T)^{-1}$ and μ is the chemical potential. It is determined by expressing the number of electrons $N_{\rm e}$ in terms of it, *i.e.*,

$$N_{\rm e} = \sum_{pq\sigma} \frac{1}{\exp[\beta(\epsilon_{pq\sigma}-\mu)]+1}\cdot \quad (10)$$

In practice we calculate μ by first choosing an approximate value μ_0 and calculating the corresponding value $N_{\rm e}^{(1)}$. The correction $\delta\mu_0$ to μ_0 can then be determined from

$$\delta\mu_0 = -\frac{1}{\beta}\ln\left(1+\frac{N_{\rm e}^{(1)}-N_{\rm e}}{a(T)}\right)\cdot \quad (11)$$

This expression is more convenient for numerical calculations than its linearized version in $(N_{\rm e}^{(1)} - N_{\rm e})/a(T)$ where the function $a(T)$ is given by

$$a(T) = \frac{1}{4}\sum_{pq\sigma} \cosh^{-2}\left(\frac{\beta}{2}(\epsilon_{pq\sigma}-\mu_0)\right). \quad (12)$$

One can use the corrected potential $\mu_1 = \mu_0 + \delta\mu_0$ in order to calculate the next correction $\delta\mu_1$. We obtain with $\delta\mu_1$ the chemical potential already with an accuracy of order $N^{-2}M^{-2}$, which perfectly serves our purposes.

The same procedure can be applied to carbon nanotubes. In that case the unit cell contains four carbon atoms. Hence the excitation energies form four bands, *i.e.*,

$$\epsilon_{pq\sigma}(\phi) = \pm\left(1+u_p \pm (u_p v_q)^{\frac{1}{2}}\right)^{\frac{1}{2}} + 2\pi^2\frac{m_{\rm eff}}{m}\,\frac{\sigma\phi}{N^2} \quad (13)$$

with

$$u_p = 2\left(1+\cos\left[\frac{2\pi}{N}(p+\phi)\right]\right)$$
$$v_q = 2\left(1+\cos\left[\frac{2\pi}{M+1}q\right]\right) \quad (14)$$

and $p = 1, ..., N;\quad q = 1, ..., M$ [5,6].

3 Induced dipole moment

When an electric field is applied along the z-axis the excitation spectrum of the system can no longer be calculated exactly. Instead, approximations have to be made. Since in practice the applied electric field is very small, the density of electrons changes only slightly along the z-axis. This enables us to determine the induced density changes by using a quasi-classical approximation. Within that scheme the excitation energies depend not only on p, q and σ but on the coordinate z as well. We illustrate the approximation by considering a chain of M atoms as a simple example. The Hamiltonians is of the form

$$H_{\rm 1d} = -\sum_{n=1,\sigma}^{M-1}(a^+_{(n+1)\sigma}a_{n\sigma} + {\rm h.c.}) + ea_0F_0\sum_{n\sigma} a^+_{n\sigma}a_{n\sigma}\left(n-\frac{M+1}{2}\right)\cdot \quad (15)$$

Here a_0 is the lattice constant and F_0 is an applied electric field along the chain direction.

Exact calculations of the induced dipole moment D require an evaluation of the expression

$$D = \frac{Sp\ \hat{d}\ {\rm e}^{-\beta(H_{\rm 1d}-\mu)}}{Sp\ {\rm e}^{-\beta(H_{\rm 1d}-\mu)}} = \sum_{k=1,\sigma}^{M}\frac{(\hat{d})_{kk}}{1+{\rm e}^{\beta(E_{k\sigma}-\mu)}}\cdot \quad (16)$$

Here $\hat{d}$ is the dipole operator

$$\hat{d} = ea_0\sum_{n=1,\sigma}^{M} a^+_{n\sigma}a_{n\sigma}\left(n-\frac{M+1}{2}\right) \quad (17)$$

and $E_{k\sigma}$ denotes the excitation energies of the chain. In order to compute D from (16) we have to diagonalize $H_{\rm 1d}$ in order to find the eigenenergies and eigenfunctions of that Hamiltonian. This can be done if not more than 1 000 atoms are involved. Instead of doing that we want to use here a simpler, more effective quasi-classical scheme. In the quasi-classical approximation the excitation spectrum is of the form

$$\epsilon_{pm} = -2\cos\left[\frac{2\pi}{M+1}\,p\right] + ea_0F_0\left(m-\frac{M+1}{2}\right) \quad (18)$$

with $p = 1, ..., M$ and $m = 1, ..., M$. The corresponding expression for the induced dipole moment is

$$D = \frac{2ea_0}{M}\sum_{pm}\frac{(m-(M+1)/2)}{{\rm e}^{\beta(\epsilon_{pm}-\mu)}+1}\cdot \quad (19)$$

It should be pointed out that the quasi-classical approximation neglects matrix elements which lead to an energy splitting at crossing points when the electric field is turned on. Therefore a possible first-order Stark effect near those points is not taken into account and we

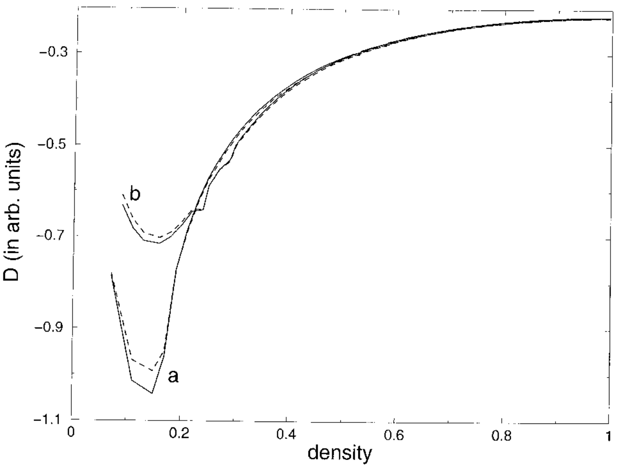

Fig. 2. Induced dipole moment as a function of electrons per site for a chain of $M = 201$ atoms calculated with the exact quantum mechanical expression (16) (dashed lines) and when a semiclassical approximation (19) (solid lines) is made. (a) and (b) correspond to temperatures $k_{\mathrm{B}}T = 0.01$ and 0.05, respectively (in units of the transfer integral).

are in the linear response regime. Despite this we have not expanded this expression in F_0 for practical reasons. We have calculated D for a chain of $M = 201$ atoms by using (16) and alternatively (18). The results are compared in Figure 2 for different densities and temperatures. The deviations caused by the semiclassical approximation are less than 1% or $\frac{1}{M}$ in all cases. This justifies the use of a quasi-classical approximation when we calculate the dielectric response of cylindrical molecules such as nanotubes in an applied magnetic field.

4 Results and discussions

In the following we want to present results for the dielectric response of the two types of cylindrical molecules described above, *i.e.*, for a square lattice rolled into a cylinder and for nanotubes. The induced dipole moment is calculated in close analogy to the one of a ring, although here the electric field F_0 is directed along the cylindrical axis. We start with the square-lattice case. In analogy to (19) the induced dipole is calculated from

$$D(\phi) = \frac{ea_0}{M} \sum_{mpq\sigma} \frac{(m - (M+1)/2)}{\mathrm{e}^{\beta[\tilde{\epsilon}_{pq\sigma}(m,\phi) - \mu(\phi)]} + 1} \qquad (20)$$

where

$$\tilde{\epsilon}_{pq\sigma}(m,\phi) = \epsilon_{pq\sigma}(\phi) + ea_0 F_0 \; (m - (M+1)/2) \qquad (21)$$

and $\epsilon_{pq\sigma}(\phi)$ is given by (8). Results for the magnetic-field dependent part $D(\phi) - D(0)$ are shown in Figure 3 for a cylinder with 200 atoms along the circumference and 1 000 atoms along the axis, *i.e.*, $N = 200$ and $M = 1\,000$, respectively.

Note that $(D(\phi) - D(0))/D(0) = (\epsilon'(\phi) - \epsilon'(0))/\epsilon'(0)$ where ϵ' is the real part of the dielectric response in the low-frequency limit. The temperature, or more precisely $k_{\mathrm{B}}T$ is 10^{-4} in units of the hopping matrix element. The chosen density corresponds to 0.74 electrons per site. One notices a rich structure as a function of the applied magnetic field. The function $(D(\phi) - D(0))/D(0)$ is symmetrical with respect to the point $\phi/\phi_0 = 1/2$. Therefore we show in the figure the dielectric response in the region $0 < \phi/\phi_0 \lesssim 1/2$ only. The continuation of these curves can be obtained by reflection. Adding a Zeeman term to the Hamiltonian (1) spoils this periodicity but the corresponding effect is rather small, *i.e.*, of the order of a few percent. The above calculations have been done without discussions of the effect of screening, which is an important factor and can diminish $D(0)$ considerably. However, it can be shown that this decrease is independent of the applied magnetic field so that the ratio $(D(\phi) - D(0))/D(0)$ remains unchanged. A detailed proof of it is left to a future publication.

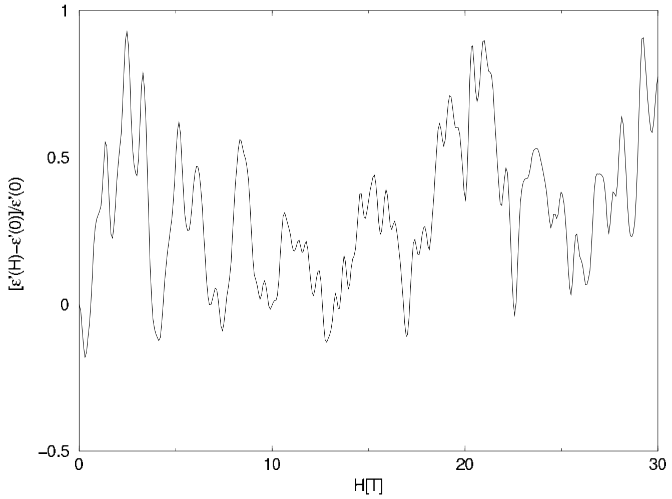

Fig. 3. Dielectric response $[\epsilon'(H) - \epsilon'(0)]/\epsilon'(0)$ for a model square-lattice system with $N = 200$, $M = 1\,000$ in an axial magnetic field. The temperature is $k_{\mathrm{B}}T = 10^{-4}$ (in units of the transfer integral), and $a_0 = 1.4$ Å. The density is 0.74 electrons per site.

A cylinder formed from a square lattice is a hypothetical case. But if one assumes a lattice constant $a_0 = 1.40$ Å as in the case of an aromatic carbon ring, the field required for the enclosure of a flux unit is of order 60 T. It is derived from the following relation between the flux ϕ (in units of ϕ_0) and the applied magnetic field

$$\phi = \frac{N^2 a_0^2 \; eH}{8\pi^2 \hbar c} \cdot \qquad (22)$$

The structure in $\epsilon'(H)$ obtained within that range of fields reflects properties of excited states, in particular crossings of energy levels.

For nanotubes the calculations are done quite similarly, but here we have to take a sum over all four energy bands. The relation between flux ϕ (in units of ϕ_0) and field H is here given by

$$\phi = \frac{3N^2 a_0^2 \; eH}{8\pi^2 \hbar c} \qquad (23)$$

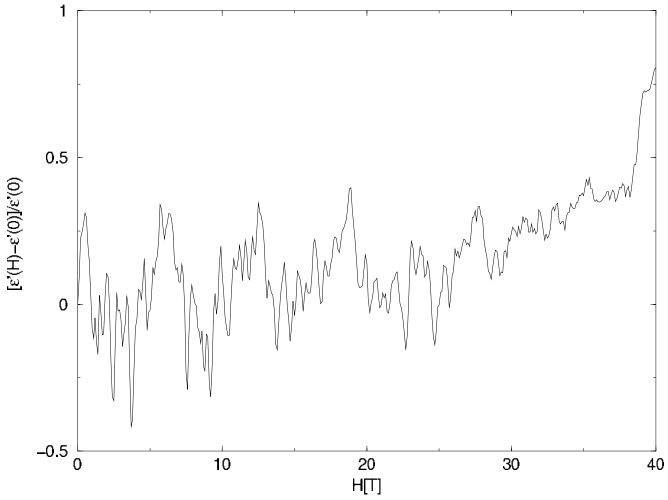

Fig. 4. Dielectric response $[\epsilon'(H) - \epsilon'(0)]/\epsilon'(0)$ for a nanotube with $N = 100$, $M = 1\,000$ in an axial magnetic field. The temperature is $k_{\mathrm{B}}T = 10^{-4}$ in units of 3 eV and the density is 0.89 electrons per site.

where N is the number of sites along the circumference and a_0 is the distance between neighboring sites. The computational results are shown in Figure 4 for a density of $n = 0.89$ π-electrons per site. One notices that the rich structure in $\delta\epsilon'(H)/\epsilon'(H)$ in the region $0 < H < 40$ T is of order unity and therefore should be easily detectable. Results for other densities look similarly, except for $n = 1$ which is special. The reason is that a honeycomb or graphite lattice has for $n = 1$ a Fermi surface consisting of a point. Therefore in a finite system the level spacing close to the Fermi energy is particularly large. This leads to small changes in $\delta\epsilon'(H)/\epsilon'(0)$ only. The situation changes at high magnetic fields. Due to the Zeeman term in the Hamiltonian the spin-dependent densities n_σ differ more and more from each other, *i.e.*, $n = n_\uparrow + n_\downarrow$ with $n_\uparrow(H) \neq n_\downarrow(H)$ and the Fermi surface moves away from the special point at half filling. This brings us back to the doped case and we obtain again a rich structure in $\delta\epsilon'(H)/\epsilon'(0)$ like in Figure 4.

In order to demonstrate that we are in the linear dielectric response regime we have calculated $(D(\phi) - D(0))/D(0)$ for two different electric fields F_0, *i.e.*, for 10 V/cm and 20 V/cm and found that this ratio remains unchanged. In collaboration with S. Pleutin we have also performed quantum calculation instead of quasi-classical ones for the cylinder derived from a square lattice (to be published). They support the quasi-classical approximation made here.

5 Conclusions

The above calculations show that large molecules of cylindrical or circular shape should show detectable magnetic field effects due to the Bohm-Aharonov effect. They lead to a strong variation of the dielectric function in the low-frequency limit as function of the applied magnetic field. Those variations are predominantly caused by doubly degenerate ground states resulting from level crossings in the applied field. At a crossing point an applied electric field causes a discontinuity in the dielectric response due to the difference in the coefficient of the quadratic Stark effect of the two levels. It may also cause a linear Stark effect instead of a quadratic one. In that case nonlinear electric field effects appear. However, in the quasi-classical approximation made here these effects are neglected. It should be pointed out that the calculated quantity $(D(\phi) - D(0))/D(0)$ is quite sensitive to the density of electrons, size of the system, electron correlations, temperature, etc. The purpose of our investigation is to show that the effect are very large and controllable. Once experiments on these systems are done the calculations can be extended to the requested specific situation. The most important extensions concern the dependence of $\delta\epsilon'(H)$ on the directions of the applied magnetic and electric fields. Important is also a proper inclusion of electron correlations. As pointed out before, the present calculations have been done within the one-electron approximation. Strong correlations are expected to result in modifications of the dielectric response [7,8]. The magnetic field dependence of the polarizability of a disordered system has been considered before [9–11]. Finally, we also have to generalize the above theory to the case of mutually interacting molecules. This may become an important issue when plate-like molecules are forming stacks and a magnetic field is applied along the direction of the stack. Although the work presented here needs extensions of the form just described it is fair to state that the results presented here justify efforts towards a systematic investigation of the magnetic-field dependent dielectric response of ring- or cylinder shaped molecules. We feel that in the future they may develop into a spectroscopic tool for studying low-energy excitations of such systems.

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