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POLING IN TWO DIMENSIONS BY A PURELY OCTUPOLAR ELECTROSTATIC POTENTIAL: HOMOGENEITY OF THE GROUND STATE*

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We investigate an arbitrary set of point charges in two dimensions, which models a rigid molecule subject to a purely octupolar electric field poling potential imposed by a system of symmetry-adapted cylindrical electrodes. We formulate the conditions which guarantee that the minimum of electrostatic potential energy of the molecule is homogeneous, that is independent of its localization inside the poling cell. These conditions state that the molecule must be charge neutral, apolar and with an isotropic charge quadrupole moment. This result constitutes a first step towards a comprehensive classification scheme for the ground states ($T = 0$) of a set of multipolar molecules poled by electric potentials of different multipolar symmetries.

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1. Introduction

The progress in nonlinear optics over the last decades has involved development of organic molecules and materials [1]. Guided by a molecular engineering approach, the structure of materials has been tailored at different scales to optimize desirable physical properties, such as nonlinear optical susceptibilities of different orders. This research was done mainly in the

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framework of irreducible tensor algebra [2,3], where symmetry considerations play a fundamental role. In this respect, one of the most important features concerns centrosymmetry breaking as a prerequisite, at the different scales at stake, towards the occurrence of odd-rank tensor properties. Such condition should be satisfied at the molecular level as well as for their assembly in a material (from nano-size particle to bulk, depending on the targeted material scale). In the context of nonlinear optics, this rule applies to second-order nonlinear phenomena, *e.g.* second-harmonic generation and its application to imaging and, more generally, to all three-wave mixing phenomena, such as the electrooptic Pockels effect or non-degenerated sum- and difference-mixing of two incoming beams. These phenomena are indeed controlled at the upstream electromagnetic propagation scale as governed by nonlinear Maxwell equations, via the quadratic susceptibility $\chi^{(2)}$, a third-rank tensor which vanishes for centrosymmetric systems. Over the last decades, dipolar conjugated molecules [4] have served as a versatile template for NLO applications. In spite of the initial relevance of the dipolar paradigm, some of its limitations have shifted the molecular engineering research frame into the broader area of multipolar molecules [5,6]. Dipolar molecules being set apart, the next candidates sustaining non-vanishing odd-rank tensor properties are then the octupoles. Unfortunately, their non-centrosymmetric statistical orientation cannot be promoted by means of traditional dipolar poling schemes because of their vanishing dipole moment. Therefore, the design of effective octupolar orienting schemes becomes an important task. Recently, one of us has proposed a general symmetry based approach which generalizes onto a multipolar frame the earlier more restricted dipolar scheme [3].

In our recent paper [7] the topic of electrostatic field poling of octupolar molecules (octupoling) in two dimensions (2D) was addressed using the complementary methods of statistical mechanics and Monte Carlo simulations. The physical picture and simplifying assumptions were discussed, leading to a lattice model of noninteracting octupoles in 2D at the nano-scale, in the presence of an inhomogeneous electric poling field imparted by a system of cylindrical electrodes. Building up on the Laplace equation solution for the potential, we have formulated, using basic concepts of statistical mechanics, a criterion for octupoling which includes important parameters: charge distribution and linear size of the octupolar molecule, poling voltage, radius of the electrodes and temperature. It was found that a well-ordered octupolar phase appeared at very low, sub-Kelvin temperatures. This highly demanding octupoling criterion was ascribed to symmetry-driven effects which decreased the quality of the octupolar non-centrosymmetric order even in the ground state ($T = 0$), as well as to thermal fluctuations at above-zero temperatures and related numerical factors. Among these factors that relate to a potential softening of the poling requirements discussed in [7] two appear to be of primary interest. The first one is a more advanced design of the distribution of charges in the model octupolar molecule. The octupolar molecule, by definition, is represented by a set of charges $q_1, \ldots, q_n$, such that the first non-zero odd-order irreducible multipolar electric moment is the octupole. The second one requires the design of more effective electric field poling schemes which, in particular, promote a homogeneous, non-centrosymmetric octupolar order in the ground state. This work is closely related to an advanced topological classification of various ground states in the presence of topological defects (vortices) already reported in Ref. [7]. The structure of the ground state depends on the presence of various multipolar electric moments of the molecule and of multipolar components of the poling field.

The first step towards the classification of the ground state was made in our recent paper [8], where a purely octupolar ($J = 3$ in the irreducible tensor nomenclature [2]) poling potential was used (see the next section for details). We have studied a specific case whereby the octupolar molecule follows a so-called "Y" pattern octupolar design, with a set of three localized charges q, set at the vortices of an equilateral triangle, while an opposite $-3q$ compensating charge is centered to ensure neutrality (Fig. 3 (a)). In this case, the electrostatic potential energy of the molecule does not depend on the position of its center, but only on the molecule's orientation, leading to a homogeneous non-centrosymmetric ground state. However, the potential barriers preventing orientational disorder were low, leading to the thermally-driven destruction of octupolar order above a temperature threshold as low as 10^{-4} K. The emerging question is whether other designs of octupolar molecules can somewhat relax the poling conditions.

This contribution is a first step in this direction, by way of addressing a more general, but closely related topic. Its objective is to formulate the requirements for the generic molecular charge distribution for which the ground state of an ensemble of such non-interacting molecules embedded in a purely octupolar potential is homogeneous throughout the area of the poling cell.

2. Arbitrary system of point charges in a purely octupolar potential

Consider an arbitrary set of point charges $q_i,\ i = 1, 2, \ldots, n$, placed at positions $\vec{r}_i$, see Fig. 1, representing a model of a molecule in the poling cell. The values of charges and the relative distances between them are fixed. Consequently, we neglect the polarizability effects and vibrational motions of the molecule, leaving them for future studies. The electric field is imparted by a single cylindrical electrode infinite along its axis and with a circular cross-section of radius R, see Fig. 1, this being the continuous geometric limit of a set of discrete and disconnected electrodes, as further recalled (see also Ref. [3]). The perimeter of the cell is formed by the intersection of the electrodes with the (x, y) plane. The system is effectively two-dimensional because of its translational symmetry in z direction. More details can be found in Refs. [7,8].

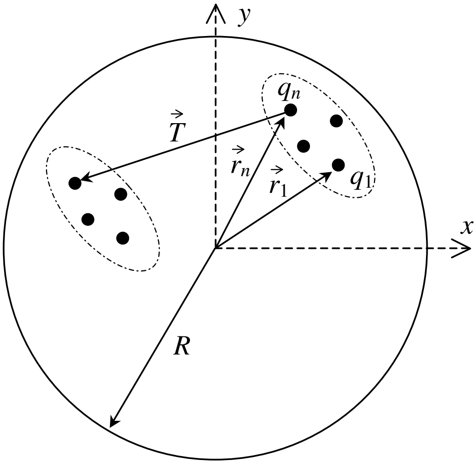

Fig. 1. Schematic view of the poling cell in (x, y) plane with a set of charges q_i located at points $\vec{r}_i$, representing a molecule in the poling cell. The set of charges translated by a vector $\vec{T}$ (see the text) is also shown. Boundary conditions for the potential are set on a circular electrode of radius R.

The electrostatic field inside the poling cell is uniquely determined by the boundary conditions, which we chose as purely octupolar, *i.e.*, with a single $J = 3$ octupolar component in the multipolar (or Fourier) expansion

$$V(R, \theta) = V_0 \sin 3\theta \,. \tag{1}$$

Inside the poling cell the potential satisfies the Laplace equation and reads [9]

$$V(r, \theta) = V_0 \left(\frac{r}{R}\right)^3 \sin 3\theta \,, \tag{2}$$

where $0 \leq r \leq R$ and $0 \leq \theta < 2\pi$ are the polar coordinates inside the poling cell, see Fig. 2. To avoid misunderstanding we point out that no continuous potential boundary condition can be implemented by means of a one-piece metallic electrode. It can nevertheless be approximated step-wise by splitting the cylinder into a set of independent electrodes [3].

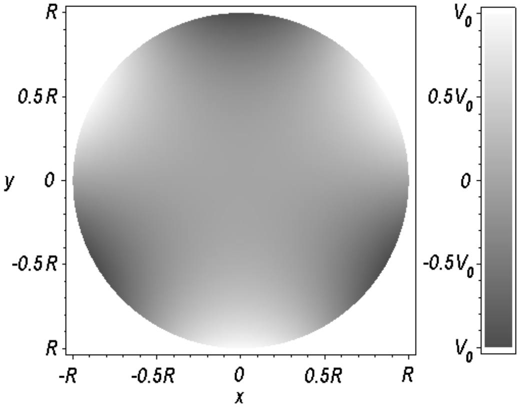

Fig. 2. Contour plot of purely octupolar poling potential inside the poling cell $V(r,\theta) = V_0\left(\frac{r}{R}\right)^3 \sin 3\theta$, Eq. (2).

In what follows, we study the effect of a pure translation of the molecule (without rotations) on its electrostatic potential energy and then formulate the conditions under which the energy is invariant with respect to arbitrary translations. For convenience, we set $V_0 = 1$ and chose R as the distance unit. The electrostatic potential energy reads

$$E = \sum_{i=1}^{n} q_i V(\vec{r}_i) + \frac{1}{2}\sum_{i=1}^{n}\sum_{j\neq i}\frac{q_i q_j}{|\vec{r}_j - \vec{r}_i|}\,. \tag{3}$$

The second term is constant because the model molecule is rigid, so we will skip it. For further studies it is more convenient to express potential $V(r,\theta)$ in the Cartesian coordinates x, y. Since

$$\sin 3\theta = 3\cos^2\theta\sin\theta - \sin^3\theta\,, \tag{4}$$

$$\sin\theta = \frac{y}{r}\,, \tag{5}$$

$$\cos\theta = \frac{x}{r}\,, \tag{6}$$

Eq. (2) (with $V_0 = 1$, $R = 1$) becomes

$$V(\vec{r}) \equiv V(x,y) = 3x^2y - y^3\,. \tag{7}$$

One way to study the conditions of invariance of the potential energy E with respect to translations is to express it as a function of the vector position of the center of mass $\vec{R}_{\mathrm{CM}}$ of the molecule and of rotation angle φ of the molecule as a whole, and next to solve the equation $\nabla_{\vec{R}_{\mathrm{CM}}} E(\vec{R}_{\mathrm{CM}}, \varphi) = 0$, where $\nabla_{\vec{R}_{\rm CM}}$ denotes gradient with respect to $\vec{R}_{\rm CM}$. This differential technique is somewhat cumbersome and we prefer to use instead discrete macroscopic translations. Namely, we calculate the change of energy, Eq. (3), when the set of charges is translated by vector $\vec{T}=[A,B]$, see Fig. 1. Let us first calculate the potential at the point $\vec{r}+\vec{T}=[x,y]+[A,B]$. Some straightforward algebra yields

$$\begin{aligned} V(x{+}A,y{+}B) &= 3(x+A)^2(y+B)-(y+B)^3 \\ &= 3x^2y-y^3+3A^2B-B^3 \\ &\quad +3\left((2AB)x{+}\left(A^2{-}B^2\right)y{+}A(2xy){+}B\left(x^2{-}y^2\right)\right) . \end{aligned} \tag{8}$$

The difference of energy ΔE between the energies of translated and the original systems then reads

$$\begin{aligned} \Delta E &= \sum_i q_i V\left(\vec{r}_i+\vec{T}\right)-\sum_i q_i V(\vec{r}_i) \\ &= 3\left(2AB\mu_x{+}\left(A^2{-}B^2\right)\mu_y{+}A\mathcal{Q}_{xy}{+}B(\mathcal{Q}_{xx}{-}\mathcal{Q}_{yy})\right){+}\left(3A^2B{-}B^3\right)Q\,, \end{aligned} \tag{9}$$

where the quantities

$$\begin{aligned} Q &= \sum_i q_i\,, & & \\ \mu_\alpha &= \sum_i q_i(\vec{r}_i)_\alpha\,, & & (\alpha\in\{x,y\})\,, \\ \mathcal{Q}_{\alpha\beta} &= \sum_i q_i(\vec{r}_i)_\alpha(\vec{r}_i)_\beta\,, & & (\alpha,\beta\in\{x,y\}) \end{aligned}$$

denote the total charge, the components of the dipole moment and the components of the electric quadrupole moment, respectively. Then, Eq. (9) straightforwardly yields the required conditions: the energy is invariant with respect to translation (*i.e.* it is independent of A, B) provided that the following relations hold

$$Q = 0\,, \tag{10a}$$

$$\vec{\mu} = 0\,, \tag{10b}$$

$$\mathcal{Q}_{xy} = 0\,, \tag{10c}$$

$$\mathcal{Q}_{xx} = \mathcal{Q}_{yy}\,. \tag{10d}$$

The first two conditions state that the molecule must be charge neutral together with a strictly cancelled dipolar moment; the last two — that the tensor of quadrupole moment must be isotropic

$$\mathcal{Q}_{\alpha\beta}\propto\delta_{\alpha\beta}\,. \tag{11}$$

Let us introduce some molecular considerations to exemplify and illustrate criterion (10), while still remaining at a generic level. There exists a large class of molecular charge distributions which satisfy this criterion, however not all of them are of interest for second-order nonlinear applications. Firstly, the prerequisite for the centrosymmetry-breaking eliminates a large class of them, leaving only three-fold symmetry (C_{3v} and D_{3h} point groups) as the only symmetry option to simultaneously meet non-centrosymmetry and the cancellation of vectorial properties such as the charge dipole moment (Refs. [5,6]). Beyond the charge quadrupole moment, the isotropy condition can then be seen to apply to any rank two tensor properties, such as for example, the linear polarizability tensor α. Indeed, an isotropic polarizability tensor is one of the additional benefits of octupolar molecules in that octupolar ordering will not influence the lower order dielectric properties which remain indeed isotropic, thus avoiding optical scattering losses due to index inhomogeneities which is a well known drawback in the usual case of "dipoling".

Secondly, the requirement of energy invariance discussed above does not necessarily bring about the homogeneity of the ground state — additional requirement is that the energy is dependent on the angle of rotation of the molecule as a whole. Those concepts are exemplified in Fig. 3, where a few chosen molecular charge distributions which satisfy Eqs. (10), are non-centrosymmetric and have an homogeneous ground state, are shown. The design in cases (a) and (b) corresponds to the third $J = 3$ step of a recursive point charge model for 2^J multipoles [10] in the 2D case: a J-order

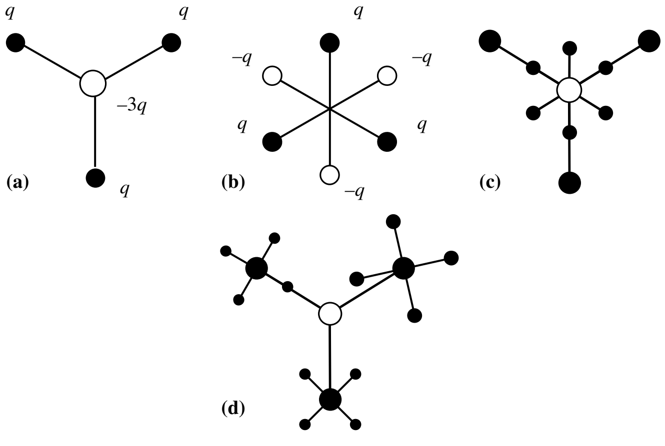

Fig. 3. Exemplary molecular charge distributions which meet criterion (10), are non-centrosymmetric and give rise to an homogeneous ground state in a purely octupolar poling potential, see the text.

multipole can be accounted for by a set of J charges of the same sign and magnitude q at the apex of a regular polygon compensated by an opposite $-Jq$ charge at the center (case (a)) or, alternatively, by a set of $2J$ regularly alternating charges at the apex of a regular polygon (case (b)). Molecular charge distribution shown in case (a) corresponds to "Y" shape paradigm and was studied in Refs. [7, 8]. Designs (c) and (d) illustrate the effect of the "decoration" of the basic pattern (a). First of them retains the three-fold symmetry of the molecule, while the second design, case (d), breaks it down. In this case, the end-points of the molecular arms were decorated with (compensated) charge distribution of the same shape but various linear dimensions and, additionally, with arbitrary orientations.

3. Conclusions

We have studied the electrostatic potential energy of a model molecule, represented by set of point charges, in a purely octupolar electrostatic potential. We have fully characterized a generic charge distribution for which the energy remains constant under the translations of the molecule as a whole, without rotations, inside the poling cell. The corresponding conditions, Eq. (10), state that the total molecular charge and dipole moment should vanish while its electric quadrupolar moment should be isotropic. Simple illustrative examples of the corresponding molecular charge design were provided and discussed. The ground state under a purely octupolar potential in the octupoling cell of a system of generic molecular patterns as displayed in Fig. 3, is homogeneous and builds-up a fully ordered non-centrosymmetric octupolar phase. Our result is of interest towards further design of model molecules, especially in the case when inter-molecular electrostatic interactions are taken into account and eventually further taken advantage of so as to improve on the octupolar ordering. The flexibility, which stems from Eq. (10), allows for a "decoration" of basic patterns and can hopefully promote such structures where the electrostatic interactions reinforce the homogeneity of the ground state, which results from the poling potential alone.

From a methodological point of view, we have targeted herein specific molecular and supramolecular properties, namely the homogeneity of the octupolar order in connection with molecular features emphasizing the role of lower order charge multipoles, up to the quadrupole for quadratic NLO properties. It is, nevertheless, to be remembered that a group theoretical approach, namely the application of irreducible group representation on tensor spaces, could "short-circuit", to some extent, more specific approaches and the related calculations, with the additional benefit of a greater generality as to the physical properties at stake. Along such general lines while bearing in mind the topic of this study, it is obvious that for an arbitrary 2D system at any scale (molecular or supramolecular) that is simply abiding to threefold symmetry, then any attached tensorial property of rank two (such as the polarizability at the molecular scale or the linear dielectric response or the index of refraction at an upscaled level) will be forced to isotropy. This will happen by sole virtue of the overall threefold symmetry constraints to which all tensor properties have to obey and which cuts off any anisotropic contribution to rank two properties. This can be easily understood by remembering that any rank two property can be accounted for by an elliptical indicatrix (the index ellipsoid in the case of the linear index of refraction). Then applying a three-fold symmetry invariance constraint to an ellipse cannot but reduce it to a circle, hence the isotropy. One could also define such an indicatrix for the quadrupole moment and then apply the same general rationale. This being stated, we believe that an approach such as developed herein, nevertheless remains not only valid but needed in order to translate general principles into more targeted molecular and intra-molecular considerations, here the quadrupole isotropy, that further define useful molecular engineering pathways and practical design rules.

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