

# Coulomb interactions of polar molecules on symmetric plane lattices

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The symmetry properties of Fourier components of multipole-expansion tensors at symmetry points of the first Brillouin zone of square and triangular lattices, along with a chain representation of the Coulomb interactions, make it possible to determine energy characteristics of orientation structures through the use of a minimum number of independent parameters. In particular, the ground state of dipoles on a complex hexagonal lattice is determined.

The orientational order of molecules adsorbed on solid surfaces or intercalated in layered crystals is determined by the nature of the adsorption potentials and the intermolecular interactions.<sup>1,2</sup> For polar molecules on insulating substrates, dipole-dipole interactions are predominant. If the molecules have a sufficient rotational mobility in the plane of the surface, these interactions give rise to homogeneous or layered orientational structures. The layered structures have a doubled lattice constant. These structures are stable with respect to thermodynamic fluctuations in a certain region of low temperatures<sup>3</sup> [an ordering of this sort at  $T < 25$  K was recently observed<sup>4</sup> in the CO/NaCl(100) system]. Orientational configurations of molecules of organic dyes on substrates are also distinguished by their diversity. Their exciton states are determined by Coulomb interactions of electronic excitations of the individual molecules.<sup>5,6</sup> There is accordingly a need for a theory of dipole interactions (and of higher-multipole interactions) on plane lattices. In contrast with direct numerical calculations (which are not of much heuristic value), such a theory would make it possible to find analytic relations between the structure of the system and various observable properties of the system. Progress in this direction was made in Ref. 7, where the use of a chain representation of the interactions revealed that the energies and structures of the ground states of dipoles, the frequencies of their orientational vibrations, and phase-transition temperatures are related in a fairly simple way to the geometric parameters of a 2D Bravais lattice.

In the present letter we describe the ground state of dipoles on a complex hexagonal lattice. We show that, for the case of adsorption potentials which tend to orient the dipoles perpendicular to the surface, the vibrational (or electronic) spectrum of the system with tilted orientations of the dipole moments is characterized by a Davydov splitting of spectral lines (by analogy with the experimental result on a square lattice<sup>4</sup>). We regard this circumstance as important, since hexagonal lattices are realized in the basal plane of graphite, and there has been extensive adsorption research for graphite substrates.<sup>8,9</sup> In addition, we will show that the characteristics of the orien-

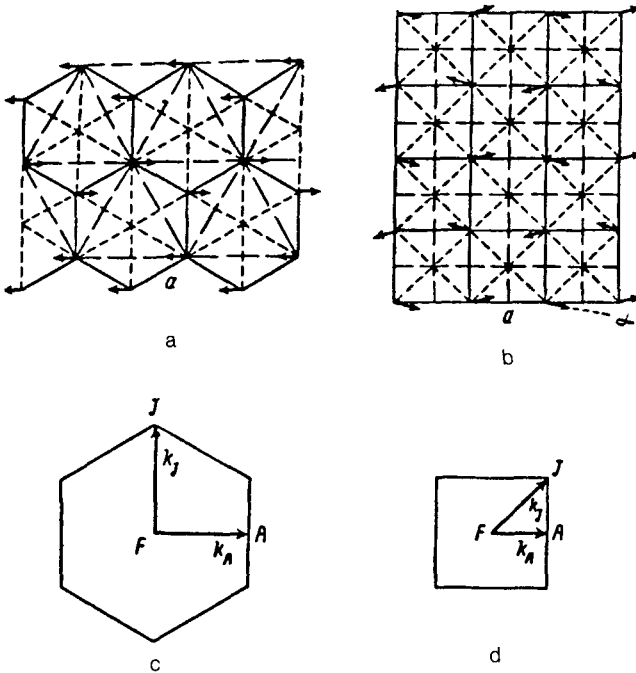


FIG. 1. Duality and similarity transformations of symmetric plane lattices. a—Structure of orientations of dipole moments in the ground state on a hexagonal lattice, along with the associated triangular lattices and sublattices; b—dual square lattices and sublattices; c and d—first Brillouin zones of triangular and square lattices.

tational ground states of dipoles on triangular and hexagonal lattices are determined by only two lattice sums, which are calculated independently. These sums can be calculated essentially exactly by taking into account only the first few terms of a series in a chain representation of interactions. The same assertion applies to a square lattice.

A chain representation of interactions of dipole lattices can be credited to Van der Hoff and Benson.<sup>10</sup> This representation was used in Ref. 11 to write, for the first time, the interaction energy of two parallel chains of dipoles with an arbitrary displacement of the nodes in the neighboring chains (the necessary equations can also be found in Refs. 1, 2, and 7). Analysis showed that it is favorable for the dipoles to become oriented along the axes of the chains with the shortest distances between nodes and to have parallel orientations in the chains with the displaced nodes (e.g., a triangular lattice) or antiparallel orientations in the chains with the undisplaced nodes (a rectangular lattice). An understanding of this behavior turns out to be sufficient for predicting the structure of dipole orientations in the ground state on a hexagonal lattice (Fig. 1a). The corresponding interaction energy can be calculated directly in the chain representation. However, it is far more elegant to relate this quantity to parameters of a triangular lattice which have already been calculated, by making use of duality and similarity considerations regarding plane lattices, which have proved

very fruitful in the statistical physics of exactly solvable models.<sup>12</sup>

It is pertinent to note that the nodes of a hexagonal lattice, for which the side of the hexagon is  $a$ , form two triangular sublattices with sides of  $a\sqrt{3}$ , and they also coincide with  $2/3$  of the sites of a triangular lattice with a side  $a$ . In this structure, each third horizontal row of sites is free of dipoles. Structures with different orientations of dipoles in sublattices of scale  $a\sqrt{3}$  can be described by a corresponding Fourier component of the interactions on a triangular lattice of scale  $a$  or by linear combinations of these components at symmetry points of the first Brillouin zone (Fig. 1c). Finally, for interactions which fall off in a power-law fashion over distance, as  $r^{-n}$  (where we would have  $n=3$  for dipole-dipole interactions), we can relate the energies of uniform structures on similar lattices of different scales and thereby find expressions for the sublattice interaction energies. The energy of a hexagonal lattice of dipoles (with dipole moments  $\mu$ ) containing  $N$  nodes in the main region is then

$$\tilde{H}_{F,A} = \frac{1}{2} N \frac{\mu^2}{a^3} \tilde{D}_{F,A}, \quad (1)$$

and the ferroelectric state ( $F$ ) and layered antiferroelectric state ( $A$ ) are governed by the minimum eigenvalues of the Fourier components of the dipole-dipole interaction tensor on a triangular lattice at the symmetry points  $\mathbf{k}=0$  ( $D_F = -5.517\ 088$ ) and  $\mathbf{k}=\mathbf{k}_A$  ( $D_A = -4.094\ 910$ ) of the first Brillouin zone:

$$\begin{aligned} \tilde{D}_F &= 2^{-1}(1+3^{-3/2})D_F = -3.289\ 426, \\ \tilde{D}_A &= 2^{-1}[3^{-1}D_F + (1+3^{-1/2})D_A] = -4.149\ 068. \end{aligned} \quad (2)$$

(Here and below, all digits except the last are exact.) The latter value is the minimum value possible. It determines the structure of the ground state shown in Fig. 1a.

In the case of dipole orientations tilted with respect to the plane of the lattice (with an angle  $\theta$  from the normal to this plane), the molecules belonging to one unit cell of the 2D crystal become orientationally nonequivalent, and the Davydov splitting of the spectral lines in two perpendicular directions is

$$\Delta\omega_{D_{av}} = \omega_{\mathbf{k}=0}^{\parallel} - \omega_{\mathbf{k}=0}^{\perp} = (\chi/a^3)\omega_0 [(\tilde{D}_F - \tilde{D}_A)\sin^2\theta - (\tilde{D}_F^z - \tilde{D}_A^z)\cos^2\theta]. \quad (3)$$

Here  $\chi$  and  $\omega_0$  are the polarizability and frequency of an individual molecule (vibrational or electronic, depending on the type of spectrum under study). The  $z$ th projections of the corresponding Fourier components are given by

$$\tilde{D}_F^z = -2\tilde{D}_F = -(1+3^{-3/2})D_F; \quad \tilde{D}_A^z = -\tilde{D}_A - \tilde{D}_{A'} = 3^{-1}D_J = 6^{-1}(3^{-1/2}-1)D_F. \quad (4)$$

Here  $\tilde{D}_{A'} (> \tilde{D}_A)$  is the second eigenvalue of the tensor under consideration for a hexagonal lattice at the point  $\mathbf{k}=\mathbf{k}_A$ . The identities  $\tilde{D}_F^z = -2\tilde{D}_F$  and  $\tilde{D}_J^z = -2\tilde{D}_J$  also hold for a triangular lattice, and we have  $\tilde{D}_A^z = -D_A - D_{A'} = D_F/3$ . Consequently, all the necessary dipole lattice sums on hexagonal and triangular lattices are expressed in terms of the two sums  $D_F$  and  $D_A$  on a triangular lattice.

Relations of the type in (3) for the Davydov splitting of the spectrum of a system with dipole moments tilted with respect to the plane of a rectangular or square lattice

were found in Refs. 13 and 14. As  $D$ , they contained lattice sums of the corresponding lattices. Applying duality and similarity transformations like those used above to square lattices with scales of  $a$ ,  $2a$ , and  $a/\sqrt{2}$  (Fig. 1b), we find the following relations between the lattice sums at symmetry points of the first Brillouin zone (Fig. 1d):

$$\begin{aligned} D_F^z &= -2D_F, \quad D_A^z = -D_A - D_{A'} = 2^{-1}(2^{1/2} - 1)D_F, \quad D_J^z = -2D_J = (2 - 2^{1/2})D_F, \\ D_F &= -4.516\ 811, \quad D_A = -5.098\ 873. \end{aligned} \quad (5)$$

These values also determine the structure of stable configurations of dipoles of a square lattice in an external electric field.<sup>15</sup> Consequently, all the resulting relations for the problems mentioned in this letter can be expressed in terms of two independent lattice sums:  $D_F$  and  $D_A$ .

We note in conclusion that the chain representation of dipole interactions used for an exact calculation of  $D_F$  and  $D_A$  on various lattices can be generalized to the case of Coulomb interactions of two linear subsystems with an arbitrary charge density  $\rho(x)$  which are a distance  $y_0$  apart and which are displaced a distance  $x_0$  along the  $x$  axis:

$$U(x_0, y_0) = \int \int_{-\infty}^{\infty} \frac{\rho(x)\rho(x')dx dx'}{[(x_0 + x - x')^2 + y_0^2]^{1/2}} = 4\pi \int_{-\infty}^{\infty} |\rho_k|^2 e^{ikx_0} K_0(|ky_0|) dk \quad (6)$$

[ $K_0(z)$  is the modified Bessel function]. This generalization makes it a simple matter to achieve some progress toward an analytic description of the results for higher-order multipole corrections. In particular, the lifting of the degeneracy with respect to the angle  $\alpha$  of a ground state with a vortex structure

$$H_A = \frac{1}{2} N \frac{\mu^2}{a^3} [D_A + (b + c \sin^2 2\alpha)\xi^2] \quad (7)$$

(Fig. 1b;  $\xi$  is the ratio of the linear dimension of the polar molecule to the lattice constant of the square lattice,  $a$ ), which was studied in Ref. 16, can be supplemented with exact values of the coefficients  $b$  and  $c$ :  $b = 2.660\ 767$  and  $c = 13.534\ 243$ .

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