DIPOLE INTERACTIONS IN NANOSYSTEMS

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Abstract
The dipole-dipole interaction influences nanoscopic matter by fixing the patterns of permanent, displacive, and induced dipole moments, subject to constraints of molecular size and other short range interactions. Prediction of these arrangements is a challenging problem. The eigenvector of maximum eigenvalue of the dipole-dipole interaction matrix can provide insights and sometimes a complete solution. As an example, the octahedral tilt instabilities of perovskite-type crystals is shown to optimize dipolar interactions. Therefore this instability can be designated as antiferroelectric, because dipole-dipole interactions are a dominant driving force.

Keywords: dipole interaction, Clausius-Mossotti, ferroelectric, antiferroelectric, octahedral tilt, nanosystem

1. Introduction

In condensed matter one finds three kinds of electrical dipoles: (1) permanent (as in a molecular cluster of polar molecules, such as CH$_3$Cl), (2) displacive (as in BaTiO$_3$), and (3) induced (a cluster of benzene molecules in an external field). The unifying feature is that the dipole moments feel each other. Their magnitudes and orientations depend on where the other dipoles are, in a self-consistent fashion. This paper argues that one should study the linear algebra, and particularly the eigenvector of maximum eigenvalue, of the dipole-dipole matrix $\Gamma$ which relates the induced electric field $\vec{F}_{i,\text{ind}}$ at the $i$'th site $\vec{R}_i$ to the dipoles $\vec{\mu}_j$ at sites $\vec{R}_j$:

$$F_{i\alpha,\text{ind}} = \sum_{j\beta} \Gamma_{i\alpha,j\beta} \mu_{j\beta},$$ (1)

*permanent address
\[ \Gamma_{\alpha,\beta} = \frac{3 R_{\alpha,\beta} R_{\beta} - \delta_{\alpha,\beta} R_{ij}^2}{R_{ij}^3}, \]  

(2)

where \( \vec{R}_{\alpha,\beta} = \vec{R}_\alpha - \vec{R}_\beta \). The insights obtained from the eigenvectors and eigenvalues are illustrated below in some simple examples, and in an application to real materials with spontaneous electrical polarity, the octahedral tilt instability of ReO₃-type perovskite crystals.

Of course, it must be acknowledged that not all properties of polar matter have much to do with the dipole moments of their molecules. For example, the water molecule has a dipole in vapor phase, and electrical polarity is a dominant effect in the interactions of water molecules with each other and with dissolved species. However, for near-neighbor pairs, it is not a good approximation to replace the polar charge distribution of water by a single dipole. A better approximation would use two dipoles, located along the two bonds, each pointing away from the oxygen toward one of the two hydrogens. The sum of these two dipoles is the total measured dipole moment of the water molecule. Also, it would be not a very good approximation to assume that the two dipole moments of the water molecule are unchanged in their various chemical environments. Induced polarity should be treated on top of permanent or displacive polarity, and this is done in the case of the octahedral tilt. A complete theory would not make any type of dipolar approximation, but would deal with the actual varying charge distribution of the molecules in detail. Modern density functional theory does this well, but slowly, which motivates a search for a less complete but still sensible theory.

2. One Polarizable Molecule

The energy of a single molecule is \( \mu^2 / 2\alpha - \vec{\mu} \cdot \vec{F}_{\text{ext}} \) where \( \alpha \) is the polarizability and \( \vec{F}_{\text{ext}} \) is an externally applied field. The actual dipole moment \( \vec{\mu} \) is fixed by the condition that the energy is minimum, which gives \( \vec{\mu} = \alpha \vec{F}_{\text{ext}} \).

3. More than One Polarizable Molecule

Now consider \( N \) molecules, approximated as points, at chosen fixed positions \( \vec{R}_i \). It costs energy \( \mu_i^2 / 2\alpha \) to create a dipole \( \vec{\mu}_i \) on the \( i \)th site, but one gets back energy \( -\vec{\mu}_i \cdot \vec{F}_i \) from the total field \( \vec{F}_i = \vec{F}_{i,\text{ind}} + \vec{F}_{i,\text{ext}} \) at the site, where \( \vec{F}_{i,\text{ext}} \) may be spatially inhomogeneous, varying from site to site. The total energy, in a standard vector space notation, is

\[ U(\vec{\mu}_1, \ldots, \vec{\mu}_N) = \frac{1}{2} \left< \mu \left| \left( \frac{1}{\alpha} - \Gamma \right) \right| \mu \right> - \left< \mu | \vec{F}_{\text{ext}} \right>. \]  

(3)
When there are \( N \) sites, each with a dipole, then \( |\mu> \) is a \( 3N \) column vector containing all the components \( \mu_{i\alpha} \) for \( \alpha = x, y, z \) and \( i = 1, \ldots, N \). Notice that the interaction energy \(-\vec{\mu}_i \cdot \vec{F}_{i,\text{ind}}\) is reduced by a factor of 2 in the total energy, to avoid double counting. With no external field, the system is stable if \( 1/\alpha - \Gamma \) is a positive operator. Equivalently, all eigenvalues of \( \Gamma \) should be less than \( 1/\alpha \).

Just as for the single molecule, the induced dipoles \( \vec{\mu}_i \) should minimize the total energy, \( \partial U/\partial \mu_{i\alpha} = 0 \). The solution is

\[
|\mu> = \left( \frac{1}{\alpha} - \Gamma \right)^{-1} |F_{\text{ext}}> \tag{4}
\]

This is a generalized version of the Clausius-Mossotti law [1–3]. An alternate notation, \( |\mu> = \sum (1/\alpha - \gamma)^{-1} <\gamma|F_{\text{ext}}> |\gamma> \) uses an expansion in eigenvectors, where \( |\gamma> \) is the eigenvector of \( \Gamma \) with eigenvalue \( \gamma \). If the overlap \( <\gamma_{\text{max}}|F_{\text{ext}}> \) is not zero, the eigenvector of largest eigenvalue \( \gamma_{\text{max}} \) may dominate the response.

If \( \gamma_{\text{max}} \) increases to become equal to \( 1/\alpha \), then the system becomes unstable. It will develop a spontaneous polarization, with a pattern \( |\mu> \) proportional to the corresponding eigenvector \( |\gamma_{\text{max}}> \). Higher order terms not considered here are needed to determine the magnitude of the spontaneous moment.

### 4. Two Dipoles

For pedagogical purposes, let us examine the \( 6 \times 6 \) matrix \( \Gamma \) which describes the interaction between two dipoles separated by distance \( |\vec{R}| = \alpha \); to be specific, let \( \vec{R} \) point along the \( \hat{z} \) axis. Even without writing the matrix, we can find all six eigenvectors by simple physical reasoning. The eigenstates of \( \Gamma \) are those patterns of dipoles such that the induced field at each dipole is parallel and proportional to the dipole itself. Consider the patterns in Fig. 1.a-d. The field \( \vec{F}_1 \) lies along the \( z \)-axis if \( \vec{\mu}_2 \) points along \( z \), and lies in the \( xy \) plane antiparallel to \( \vec{\mu}_2 \) if \( \vec{\mu}_2 \) lies in the \( xy \) plane. Therefore vectors lying along \( \hat{z} \) separate from those lying in the \( xy \) plane, and by cylindrical symmetry, eigenvectors in the \( xy \) plane are doubly degenerate. The degenerate pair can be chosen so that one lies along \( \hat{x} \) and one along \( \hat{y} \). To save space, we project the problem onto the 2d \( xz \) plane. The resulting \( 4 \times 4 \) matrix is

\[
\Gamma = \frac{1}{\alpha^3} \begin{pmatrix}
0 & 0 & 2 & 0 \\
0 & 0 & 0 & -1 \\
2 & 0 & 0 & 0 \\
0 & -1 & 0 & 0
\end{pmatrix} \tag{5}
\]
The eigenvalues are \( (2, 1, -1, -2) \) in units of \( (1/a^3) \), and the corresponding eigenvectors, shown in Fig. 1a-d, are

\[
|a> = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}; \quad |b> = \begin{pmatrix} 0 \\ -1 \\ 0 \\ 1 \end{pmatrix}; \quad |c> = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \end{pmatrix}; \quad |d> = \begin{pmatrix} -1 \\ 0 \\ 1 \\ 0 \end{pmatrix}.
\]  

These eigenvectors all have different symmetries. Under inversion and mirror reflection in the central \( xy \) plane, the vectors have \( (\lambda_i, \lambda_m) = (--) \), \((+-) \), \((-+) \), and \((++) \) symmetry, respectively.

![Figure 1](image-url)  

*Figure 1.* Dipole patterns of two and three interacting dipoles. In a-d the eigenvectors of \( \Gamma \) are shown for two dipoles. In e,f,h, the eigenvector of largest eigenvalue is shown for three dipoles. In e, the dipoles all have equal length. In g and h the optimal patterns (not eigenvectors!) for fixed length dipoles are shown, nearly agreeing with the eigenvectors of f and h. The vectors in h and i differ in angle by about \( 3^\circ \).

The isotropic Heisenberg interaction \( U = J \vec{\mu}_1 \cdot \vec{\mu}_2 \) for two spins has exactly the same eigenvectors but very different eigenvalues. For \( J < 0 \) (ferromagnetic exchange), states a and c are low energy states, equal in energy, and states b and d are high energy states, also equal in energy. For \( J < 0 \) (antiferromagnetic exchange), the reverse is true. For magnetic systems (the \( \text{O}_2 \) molecule is a nice example), the exchange energy is much larger than the dipole-dipole interaction. The ground state of \( \text{O}_2 \) has two outer electrons, polarized ferromagnetically (\( S = 1 \)), and only a tiny spin-orbit-induced preference for the moment to point perpendicular to the axis. By contrast, electrical dipoles have a large dipole-dipole interaction which is intrinsically anisotropic and strongly prefers state a.
5. Three Dipoles

In the two-dipole problem of the previous section, the eigenstates all had the property that each molecule’s moment $\vec{\mu}_i$ (where $\mu_{i\alpha} = <i\alpha|\gamma>$) had the same magnitude $|\vec{\mu}_i|.$ This brings a nice benefit: these patterns tell us also about the energetics of the problem of fixed size permanent dipoles.

Fig. 1.e-i shows geometries and corresponding dipole patterns for three molecules. The physical situations of interest are (1) polarizable molecules with no permanent moment, (2) permanent dipoles which can orient in space but not change their magnitude, and (3) permanent dipoles which are also polarizable and change their magnitude. We omit category (3) for now. Category (1) is mathematically simplest because linear algebra determines what happens in an external field, and whether spontaneous polarity appears. Fig. 1.e,f,h show the eigenvectors of largest eigenvalue of $\Gamma$ for (e) the equilateral triangle, (f) the linear arrangement, and (h) an obtuse isosceles triangle. For the equilateral case, the eigenvector is determined by symmetry, but for the other two cases, there are two independent vectors odd under the perpendicular mirror, so a $2 \times 2$ matrix is needed, and the central atom (or molecule) has a larger $|\vec{\mu}_{ind}|$ than the end atoms.

Because $|\vec{\mu}_i|$ is no longer the same for each molecule in the maximal eigenvector, it is not the solution of the problem of a fixed moment. Instead, for fixed moments we want to know the pattern $|\mu>$ which minimizes

$$U(\vec{\mu}_1, \ldots, \vec{\mu}_N) = -\frac{1}{2} <\mu|\Gamma|\mu> - <\mu|F_{ext}>,$$

subject to $N$ nonlinear constraints $|\vec{\mu}_i| = \mu_0.$ This is a much harder mathematical problem. Fortunately, the solution is guaranteed [4] to have a smooth relation to the maximal eigenvector of $\Gamma.$ The solutions to the fixed moment problem in zero field are shown in Fig. 1.g,i, and are close to the unconstrained solutions in Fig. 1.f,h.

6. Infinite Stack of Dipoles

Consider the arrangement $|\mu>$ of Fig. 2, with equally spaced dipoles $\vec{\mu}$ of equal magnitude, all pointing in the $\hat{z}$ direction which is also the direction of the stack of molecules. It is clear that this pattern is the maximal eigenvector of the corresponding $\Gamma.$ The eigenvalue is $4\zeta(3)/a^3$ where $a$ is the spacing of dipoles and $\zeta(3) = 1.202057 \ldots$ is the Riemann zeta function. Since the moments are equal, this pattern is also the solution to the problem of fixed dipoles on a 1-d line. It is interesting to compute the electric field of this stack, which is the negative gradient of the electrostatic potential $\Phi(\rho, z)$ (where $\rho = \sqrt{x^2 + y^2}$ is the radial distance). By methods described elsewhere [4] the
potential has the asymptotic form

\[ \Phi(\rho, z) = -\frac{4\pi \mu}{a^2} \frac{\sin(2\pi z/a) e^{-2\pi \rho/a}}{\sqrt{\rho/a}} \]  

(8)

This result explains why fixed dipoles particularly like to form one-dimensional stacks. The dipole-dipole attraction within the stack is very big, and the interaction with other dipoles falls very rapidly with distance. The asymptotic form Eq.8 is already accurate to 2% at \( \rho = a. \)

7. Cubic lattice of Dipoles

An eigenvector of this problem was found independently by Clausius [1] and Mossotti [2], and is illustrated in Fig. 3. If all dipoles point along a cube axis, with equal magnitude, it is clear that the induced field does the same thing, so this is an eigenvector. The Clausius-Mossotti arguments show that the eigenvalue is \( \gamma_{CM} = 4\pi n/3 \) where \( n \), the density of molecules, is \( 1/a^3 \) for the simple cubic lattice. A good pedagogical discussion is given by Aspnes [3]. One should also ask whether this is the maximal eigenvalue. From Fig. 2, it is clear that for the simple cubic lattice illustrated in Fig. 3, the answer is “no.” One can further lower the energy by reversing the direction of alternate stacks of dipoles, producing a slightly larger eigenvalue in an antiferroelectric pattern. Luttinger and Tisza [5] proved that this pattern had the extremal eigenvalue. For diamond structure, a more complicated extremal antiferro-
electric eigenstate was found by White et al. [6]. These authors also showed that for fcc and bcc structures, the Clausius-Mossotti ferroelectric eigenstate is maximal.

8. Octahedral Tilt

Figure 3. Infinite periodic lattice of cubic symmetry, showing the ferroelectric eigenstate studied by Clausius and Mossotti. Also the 2-d analog is an eigenstate. These are not necessarily the maximal eigenstates.

Figure 4. Energy versus tilt angle for \((\pi, \pi, \pi)\) periodic tilts around the \((111)\) axis of BX\(_3\) (ReO\(_3\) structure type) perovskites. The solid line is the total electrostatic energy (units \(Z^2e^2/a\), where \(Z\) is the anion charge) computed for rigid ions comprising rigid octahedra, with a corresponding hard-core contraction perpendicular to \((111)\) planes. The dashed curves, from top to bottom, are electrostatic energy for one displaced anion, dipole-dipole attraction energy of interacting displacements, and volume contraction energy. The sum of these is the dashed curve, coinciding with the exact energy up to fourth order terms in the Taylor series.
In this last section a brief discussion is given of recent work to be explained more fully elsewhere [7–9]. We have found that dipole-dipole interactions play an unexpectedly big role in the “octahedral tilt” instabilities common in perovskite materials [10–13]. The motif is evident in Fig. 1, showing the tendency of a triangular plaquette to polarize circumferentially. In the perovskite tilt, when the axis is (111), the displaced anions create the same triangular pattern of displacive dipoles. The moment points from the new anion position to the undistorted cubic anion position. These moments interact because they create an induced field at each undisplaced site. After some thought one can conclude that this is an eigenstate of $\Gamma$, and after some calculation one can prove that it is the maximal eigenstate. There is no better way to place dipoles on the X sites of ABX$_3$ perovskite than in the pattern corresponding to this tilt. The eigenvalue $\gamma_{\text{max}} = 14.461/a^3$, is 15% bigger than $\gamma_{\text{CM}}$. The consequence is that in a rigid ion picture, the BX$_3$ simplification of the ABX$_3$ lattice is only marginally stable under electrostatic and hard sphere forces. When the anion polarizability is added to the theory [7], the structure is almost immediately unstable even for very small polarizability. The maximum eigenvalue is accidentally 5-fold degenerate. Three of the partners permit $(\pi, \pi, \pi)$ alternating tilts in any linear combination around any cube axis. These generate the distortions labeled $a^{-}b^{-}c^{-}$ in Glazer notation [10]. The Glazer distortions with + signs require tilts with $(\pi, \pi, 0)$ periodicity, which happen also to be eigenvectors of $\Gamma$, with slightly smaller than maximal eigenvalue. It seems appropriate, given the role that dipolar interactions play, to regard all these distorted ground states as multiple-sublattice antiferroelectrics. The other two partners are related to the cooperative Jahn-Teller ground state of LaMnO$_3$, which thus also has an unexpected contribution from polar interactions in its distorted ground state.

9. Summary

Maximal eigenstates of the dipole-dipole interaction tensor $\Gamma$ are useful and relevant to several problems: response of polarizable clusters to external fields, causes and patterns of spontaneous distortion of polar assemblies, and the self-organization of polar molecules in various media. It is surprising how robust and useful this concept seems to be. Given that short range repulsive forces are large, and that near-neighbor electrostatics may involve higher multipoles, there is no obvious reason why a pattern like the perovskite octahedral tilt should have to conform to the maximal eigenvector. The fact that it does should encourage us to use this tool in other problems.
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References

[1] R. Clausius, *Die Mechanische Warmtheorie* II, 62 Braunschweig (1897).
[2] O.F. Mossotti, Memorie Mat. Fis. Modena 24, 49 (1850).
[3] D. E. Aspnes, Am. J. Physics 50, 704 (1982).
[4] P. B. Allen, J. Chem. Phys. (in press); cond-mat/0307209.
[5] J. M. Luttinger and L. Tisza, Phys. Rev. 70, 954 (1946).
[6] S. J. White, M. R. Roser, J. Xu, J. T. van der Noordaa, and L. R. Corruccini, Phys. Rev. Lett. 71, 3553 (1993).
[7] P. B. Allen, Y.-R. Chen, S. Chaudhuri, and C. P. Grey, manuscript in preparation.
[8] S. Chaudhuri, P. Chupas, M. Wilson, P. Madden, and C. P. Grey, manuscript in preparation.
[9] Y.-R. Chen, V. Perebeinos, and P. B. Allen, Phys. Rev. B (in press); cond-mat/0302272.
[10] A. M. Glazer, Acta Cryst. B28, 3384 (1972).
[11] P. M. Woodward, Acta Cryst. B53, 32 (1997).
[12] C. J. Howard and H. T. Stokes, Acta Cryst. B54, 782 (1998).
[13] N. W. Thomas, Acta Cryst. B54, 585 (1998).