

Crystal Potential Formula for the Calculation of Crystal Lattice Sums¹

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A new formula is derived for the determination of the potential energy of the central unit cell of a finite crystal; this formula is called the crystal potential formula. The crystal potential formula is based on a two-center Cartesian multipole expansion. The key feature of the crystal potential formula is that it achieves a separation of the lattice geometry and multipole moments. This feature allows one to compute in a highly effective way the crystal energies as a function of the molecules contained in the unit cell. Numerical implementation is discussed, and a numerical example is given. The example mimics an organic crystal composed of dipolar molecules. It is found that the crystal environment may create local minima and that the effects of the environment might be well-approximated by consideration of the proximate unit cells only. Both of these effects have important implications for the crystal engineering of molecular organic materials.

Madelung constants provide a measure for the lattice energy of inorganic crystalline solids, and they play a central role in their description.² The electrostatic interactions of extended lattice structures also are becoming more fully understood, and this knowledge is now being exploited in the design of inorganic films.³ The computation of lattice energies becomes more difficult for molecular crystals that are bound by weaker interactions, and such methods are only just emerging.^{4–6} One of the more successful approaches toward the engineering of organic molecular crystals consists of the synthon approach.^{7,8} Synthons are molecular fragments designed to recognize certain other atoms or functional groups with high selectivity and high affinity. The application of knowledge about the preferential formation of interactions between certain pairs of synthons provides a first step toward the design of crystals. Most current applications of the synthon approach focus on these primary interactions, and secondary interactions between synthons are either neglected or considered only in a much less comprehensive fashion. Since synthons basically are characterized by their electrostatic field, increasingly sophisticated approaches require the consideration of more and more secondary and higher electrostatic interactions and also require are more and more accurate description of the multipole moments of each synthon. With a view to interesting novel materials, polar molecules are particularly important, and they often produce the most useful molecular organic materials⁹ if these molecules crystallize in a fashion that results in a large macroscopic polarization. For example, most nonlinear optical materials^{10,11} contain dipolar chromophores, and noncentrosymmetry is a minimal requirement for the crystal to show nonlinear optical effects. In fact, rather large macroscopic polarizations are desirable and the manufacture of such materials has presented a grand challenge since dipolar molecules in general prefer to pack in a way that minimizes or even cancels molecular dipoles.

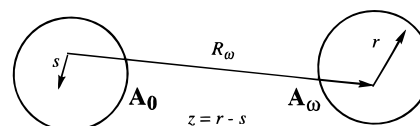


Figure 1. Definition of the local coordinate system.

In order to facilitate the manufacturing of organic molecular crystalline materials, we would like to obtain an a priori method for determining if a given molecule has a stable crystal state. We start with the potential energy function given by eq 1. The meaning of the terms in this equation are illustrated in Figure

$$\int_{A_0} \int_{A_\omega} \frac{\sigma_2(r) \sigma_1(s)}{|R_\omega + (r - s)|} dr ds \quad (1)$$

1. The regions A_0 and A_ω represent the boundaries of the molecule contained in the central unit cell and in the unit cell indexed by ω ; R_ω is the vector that starts in the center of the central unit cell and ends in the center of the unit cell indexed by ω ; r and s are vectors that start at the centers of their respective unit cells and end at some other point within their respective unit cells; and σ_1, σ_2 are charge distributions that will be defined more precisely later in the paper. We can expand eq 1 in an infinite series whose coefficients are multipole moments. Using this expansion, we would like to compute the potential energy of the central unit cell of a hypothetical crystal that is defined in terms of multipole moments (that correspond to a real molecule) and by the shape of our unit cells. To accomplish this task we need to evaluate a sum of the form given in eq 2. In eq 2, Ω is a finite collection of unit cell indices, m_i are multipole moments in the unit cell, and $f(\omega, m_1,$

$$E_{\text{pot}} = \sum_{\omega \in \Omega} f(\omega, m_1, \dots, m_k) \quad (2)$$

... m_k) is the approximate (since we are only dealing with finitely many multipole moments) potential energy of the central

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unit cell of the crystal with the unit cell indexed by ω . Since the above sum is over all the unit cells in the crystal, and since the number of unit cells grows cubically with the volume of the crystal, performing the above sum is practical only for very small crystals. Several methods exist that can be used to reduce the computational complexity of calculating eq 2. The most widely known methods are the Ewald methods and these methods have been reviewed.¹² Other methods are multipole methods,^{13–15} extrapolation and convergence acceleration methods,^{16,17} and Euler Maclaurin summation.^{18,19} Since we are looking for stable states we need to find the relative minima of eq 2 with respect to geometry and orientation of the multipole moments. One approach for finding the relative minima is to simply vary our parameters (manually or via some search algorithm) and see where minima occur. The drawback to this approach is that eq 2 has to be recalculated every time the parameters change. In order to overcome this computational bottleneck, we have developed a method that separates the lattice geometry and the multipole moments. As a result we can rotate our multipole moments and, as long as our geometry remains constant, recalculate eq 2 without performing any major calculations.

We first derive the multipole–multipole potential energy formula. We start our derivation by expanding $|R_\omega + z|^{-1}$, the reciprocal of the distance between a point in A_0 and a point in A_ω , in an infinite series expansion as follows:

$$|R_\omega + z|^{-1} = |R_\omega|^{-1} \left(1 + \frac{2z \cdot R_\omega}{|R_\omega|^2} + \frac{|z|^2}{|R_\omega|^2} \right)^{-0.5} \quad (3)$$

Setting $x = (2z \cdot R_\omega)/|R_\omega|^2 + |z|^2/|R_\omega|^2$ and applying the appropriate expansion formula, we find that $|R + z|^{-1}$ has a power series expansion of the form

$$|R_\omega + z|^{-1} = |R_\omega|^{-1} \left(1 + \sum_{n=1}^{\infty} a_n x^n \right) \quad (4)$$

whenever $|x| < 1$, and where

$$a_n = \frac{-(1)^n (2n-1)!}{n! (n-1)! 2^{2n-1}}$$

With a little calculation it can be shown that

$$x^n = |R_\omega|^{-2n} \sum_{k=0}^n \binom{n}{k} 2^{n-k} \langle (\otimes^k I) \otimes (\otimes^{n-2k} R_\omega), \otimes^{n+k} z \rangle \quad (5)$$

where I is the 3 by 3 identity matrix, \otimes^k is the k -fold tensor product, and $\langle \dots \rangle$ is the inner product operator. If we replace z by $(r - s)$ and rearrange the terms, we get

$$\frac{1}{|R_\omega + (r - s)|} = \frac{1}{|R_\omega|} + \sum_{m=1}^{\infty} \sum_{k=0}^{\lfloor m/2 \rfloor} \langle \sum_{k=0}^m b(\omega)_{m-k,k} A(\omega)_{m-k,k}, \otimes^m (r - s) \rangle \quad (6)$$

where

$$b(\omega)_{j,k} = |R_\omega|^{-2j-1} a_j 2^{j-k} \binom{j}{k}; A(\omega)_{j,k} = (\otimes^k I) \otimes (\otimes^{j-2k} R_\omega)$$

If we denote the electron density distribution of a molecule on A_0 as $\rho(r)$ and the charge of nucleus i , located at P_i , as q_i , then

TABLE 1. Values of m versus Multipole–Multipole Interactions

	m				
	monopole	dipole	quadrupole	octupole	hexadecapole
monopole	0	1	2	3	4
dipole	1	2	3	4	5
quadrupole	2	3	4	5	6
octupole	3	4	5	6	7
hexadecapole	4	5	6	7	8

we can define the “charge distribution” $\sigma(r)$ by

$$\sigma(r) = \rho(r) + \sum_i q_i \delta_{P_i}(r)$$

where the Dirac delta function δ has the property

$$\int_A \delta_{P_i}(r) = 1 \text{ if } P_i \in A, \text{ and } \int_A \delta_{P_i}(r) = 0 \text{ if } P_i \notin A$$

If σ_1, σ_2 are molecular “charge distributions” within the unit cells, then the potential felt by the central unit cell due to σ_1 in the central cell and σ_2 in the cell indexed by ω becomes

$$\int_{A_0} \int_{A_\omega} \frac{\sigma_2(r) \sigma_1(s)}{|R_\omega + (r - s)|} dr ds = \frac{1}{|R_\omega|} \int_{A_0} \sigma_1(s) ds \int_{A_\omega} \sigma_2(r) dr + \sum_{m=1}^{\infty} \sum_{k=0}^{\lfloor m/2 \rfloor} \langle \sum_{k=0}^m b(\omega)_{m-k,k} A(\omega)_{m-k,k}, \int_{A_0} \int_{A_\omega} \sigma_2(r) \sigma_1(s) (\otimes^m (r - s)) dr ds \rangle \quad (7)$$

The right-hand side of equation 7 can be turned into an expression of monopoles, dipoles, quadrupoles, ... etc., by simply expanding the tensor product and appropriately interchanging the integration. For example, if $m = 2$, the (i, j) component of

$$\int_{A_0} \int_{A_\omega} \sigma_2(r) \sigma_1(s) (\otimes^2 (r - s)) dr ds$$

is given by eq 8.

$$\begin{aligned} & \left(\int_{A_0} \sigma_1(s) ds \right) \left(\int_{A_\omega} \sigma_2(r) r_i r_j dr \right) \\ & - \left(\int_{A_0} \sigma_1(s) s_j ds \right) \left(\int_{A_\omega} \sigma_2(r) r_i dr \right) \\ & - \left(\int_{A_0} \sigma_1(s) s_i ds \right) \left(\int_{A_\omega} \sigma_2(r) r_j dr \right) \\ & + \left(\int_{A_0} \sigma_1(s) s_i s_j ds \right) \left(\int_{A_\omega} \sigma_2(r) dr \right) \quad (8) \end{aligned}$$

Equation 8 is an expression of monopole, dipole, and quadrupole components. Thus we have derived an expression for the multipole–multipole potential. See Table 1.

Since we want to determine the value of the potential energy E_{pot} , we need to sum the right-hand side of eq 7 over all $\omega \in \Omega$. We introduce the following notation. Let Ω_k be a crystal with k unit cells, define $C_0(\Omega_k) = \sum_{\omega \in \Omega} |R_\omega|^{-1}$ and $C_m(\Omega_k) = \sum_{\omega \in \Omega} \sum_{k=0}^{\lfloor m/2 \rfloor} b(\omega)_{m-k,k} A(\omega)_{m-k,k}$, where R_ω is the distance from the central unit cell to the unit cell indexed by ω , $b(\omega)_{j,k} = |R_\omega|^{-2j-1} a_j 2^{j-k} \binom{j}{k}$, and $A(\omega)_{j,k} = (\otimes^k I) \otimes (\otimes^{j-2k} R_\omega)$. It is easy to see that all geometric information is contained within the constants $C_m(\Omega_k)$. We now sum the right-hand side of eq 7

over all $\omega \in \Omega$ and then interchange the sums to get the following

$$E(\sigma_1, \sigma_2) = C_0(\Omega_k) \int_{A_0} \sigma_1(s) ds \int_{A_\omega} \sigma_2(r) dr + \sum_{m=1}^{\infty} \langle C_m(\Omega_k), \int_{A_0} \int_{A_\omega} \sigma_2(r) \sigma_1(s) (\otimes^m(r-s)) dr ds \rangle \quad (9a)$$

We call eq 9a the *crystal potential formula* (CPF). In this equation the geometry (i.e., the C_m) and the charge distributions are completely independent of each other. The equation for E_{pot} can now be written as

$$E_{\text{pot}} = \sum_{ij} E(\sigma_i, \sigma_j) \quad (9b)$$

where the sum is taken over all the σ_i, σ_j pairs in the unit cell. Equation 9 represents an efficient method of evaluating a large number of finite crystals with fixed geometry.

To demonstrate the importance of this concept, we examine a special case where the unit cell contains only one dipole moment μ while all the multipole moments are zero. In this case eq 9 simplifies to eq 10.

$$E_{\text{pot}} = \langle C_2(\Omega_k), -2(\mu_i \mu_j)_{i,j=1,2,3} \rangle \quad (10)$$

Changing the value of the dipole vector μ will not effect the value of $C_2(\Omega_k)$. Thus once $C_2(\Omega_k)$ has been calculated, the size of the lattice is no longer a computational factor. One need only to define μ and evaluate eq 10.

For large crystals the computation of C_m can be a very nontrivial problem. As the volume of the crystal grows, the error due to numerical roundoff and the number of calculations required grow very rapidly. In order to ameliorate these problems, we propose using an Euler Maclaurin summation approach. Euler Maclaurin methods in three dimensions have until recently been impractical to implement; however, recent advances in symbolic integration software have made this approach very appealing. We will present this technique in an upcoming paper.

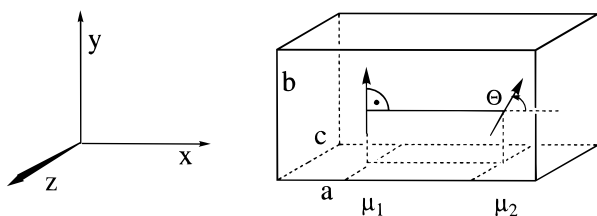


Figure 2. Depiction of the model crystal that was numerically evaluated.

To demonstrate the efficiency of the computation of the potential energy via the crystal potential formula, we have numerically evaluated the energy of a model crystal with the unit cell shown in Figure 2. The tetragonal unit cell is $a = 6 \text{ \AA}$ long, $b = 3 \text{ \AA}$ wide, and $c = 3 \text{ \AA}$ deep and contains two dipoles of equal magnitude, $\mu_1 = \mu_2 = 1 \text{ D}$, which are located at positions $(0.25a, 0.5b, 0.5c)$ and $(0.75a, 0.5b, 0.5c)$ and these dipoles are coplanar and lie in the plane where $z = 0.5c$. One of the dipoles, μ_1 , is aligned with the b -axis (angle with a -axis is 90°) while the other dipole, μ_2 , is rotated around the z -axis by an angle of Θ . For $\Theta = +90^\circ$, this model crystal represents a completely dipole parallel-aligned ensemble. We recently succeeded in the fabrication of two prototypes of near-perfectly dipole parallel aligned organic molecular ferroelectric materials,

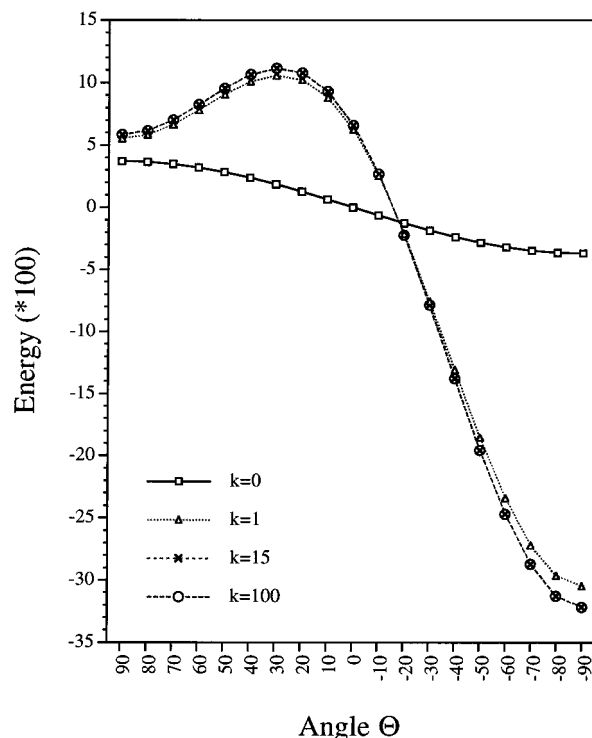


Figure 3. Energy of the central unit cell, E_{pot} , as a function of the Θ angle for crystals of various sizes ($k = 0, 1, 15, 500$).

and we are therefore particularly interested in such lattices.²⁰ On the other extreme, for $\Theta = -90^\circ$, the unit cell generates a crystal that contains layers of completely parallel-aligned dipoles in such a way that the polarizations of neighboring layers cancel. We computed $C_2(\Omega_k)$ (i.e., the dipole term) for such hypothetical rectangular crystals with $k = 0, 1, 15$, and 100 shells. These computations require only the unit cell dimensions and the locations at which the dipoles are centered (while neither the direction nor the magnitude of the dipoles enters this calculation). These $C_2(\Omega_k)$ constants are then employed to compute E_{pot} for various relative orientations of μ_1 and μ_2 . The results of our computations are graphically displayed in Figure 3. Several important conclusions have resulted. For the unit cell alone, it is clear that the dipole antiparallel alignment with $\Theta = -90^\circ$ is the only minimum of the electrostatic energy as a function of the Θ angle while the parallel alignment corresponds to an energy maximum. The situation drastically changes when the effects of the crystal environment are considered: A maximum occurs for intermediate Θ values (around 20°), and a two-minimum scenario is created. While dipole antiparallel alignment with $\Theta = -90^\circ$ becomes more and more favored as the size of the crystal increases, the dipole parallel alignment with $\Theta = 90^\circ$ becomes somewhat destabilized, but, most importantly, this lattice architecture becomes a local minimum. This simple example demonstrates the very possibility of realizing in a crystal environment a highly anisotropic dipole distribution even for cases where the dipole assembly contained in the unit cell is repulsive! Once a molecule is identified for which lattices with dipole antiparallel- or parallel-alignment exist as (local) minima, one can then think of ways to make the dipole parallel-aligned lattice the thermodynamically preferred phase if the molecules are designed such that they allow for additional nondipole interactions. We have described such design criteria elsewhere²⁰ in conjunction with our reports of the realization of two prototypes of ferroelectric organic materials that were designed with a view of making novel NLO materials with higher chromophore densities. The de novo design of crystals

is an undertaking of extraordinary complexity, and it is difficult to apply the scientific methods of analysis and synthesis to such complex systems.²¹ The results of our analysis suggest, however, that it might be possible to obtain valuable qualitative information about the effects of the crystal environment by way of considering relatively small assemblies. Figure 3 illustrates that the curve computed for $k = 1$ provides a surprisingly accurate qualitative description of the crystal effects in larger crystals. We have seen similar behavior in other simulations. If this hypothesis proves valid, then this analytical insight can be a tremendously useful device for the analysis and the design of crystals. With the crystal potential formula we are now in a position to test this hypothesis numerically, and extensive studies along those lines are in progress.

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Supporting Information Available: A table with the energies of the central unit cell in crystals with k shells ($k = 0, 1, 15,$ and 500) (1 page). This data is illustrated in Figure 3. See any current masthead page for ordering information and Web access instructions.

References and Notes

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