

The Electrostatic Term in Lattice-Energy Calculations: C₂H₂, CO₂, and C₂N₂

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Abstract

The widely used atom–atom approximation for evaluating intermolecular energies is deficient in its treatment of the electrostatic interactions. Lattice-energy calculations have been performed for three crystal structures with explicit incorporation of the electrostatic energy, at three levels of approximation, based on Hartree–Fock molecular charge distributions. Although the molecules chosen are all non-polar, the electrostatic term in each case provides most of the calculated lattice energy and leads to an appreciable contraction of the predicted equilibrium cell dimensions. In cyanogen the electrostatic contribution appears necessary to account for the observed orthorhombic structure rather than an alternative cubic form. Treating each molecule as a point quadrupole severely overestimates the interaction energies of nearest-neighbor molecules but for more distant neighbors agrees fairly well with more detailed models of the molecular charge distribution. Assigning point charges to the several atoms is an adequate approximation for the three systems examined but greater flexibility is likely to be required for molecules of lower symmetry.

An extensive literature on applications of the atom–atom approximation (see, for example, Kitaigorodskii, 1973; Mirsky, 1976; Fyfe & Harold-Smith, 1976*b*; Williams & Starr, 1977; Derissen & Smit, 1977) attests to the widespread success of this model for the evaluation of intermolecular forces and energies. This success supports the approximate validity of three essential postulates of the model: (a) the interaction energy of a pair of molecules may be evaluated as a sum of pairwise interactions between atoms; (b) these interatomic interactions are isotropic, usually about the atomic centers; (c) they are broadly transferable, at least within families of related molecules. Yet it is well recognized that these postulates cannot be exactly valid. In particular, they do not properly account for the electrostatic interactions between molecules, which severely violate postulates (b) and (c). Thus, the Coulomb field of an atom that is electrically polarized is highly anisotropic, and the net charge and polarization of an atom clearly depend on its bonding environment. Accordingly, several authors have pro-

posed various elaborations of the atom–atom potential for dealing explicitly with the electrostatic energy term (Fyfe & Harold-Smith, 1976*a*; Mulder & Huiszoon, 1977; Smit, Derissen & van Duijneveldt, 1977; Carozzo, Corongiu, Petrongolo & Clementi, 1978).

The derivation of an explicit electrostatic energy expression poses a formidable challenge: how can we obtain the requisite input information on the molecular charge distribution? Evidently, much of the simplicity of the atom–atom potential will be lost if we require an intensive study of each individual molecule in order to establish the details of its Coulomb field. To preserve the simplicity and generality of the model it is desirable that an attempt be made to identify transferable parameters that can adequately characterize the charge distributions of particular bonds or chemical groups. But this is a long-range program. Our present aim is far more modest: to examine what algebraic form is appropriate for approximating the intermolecular electrostatic energy. Specifically, we compare three variously idealized representations of the molecular charge distribution for the calculation of crystal lattice energies. One outcome of such a study may be a tentative indication of how detailed our knowledge of the molecular charge density must be to permit realistic evaluation of the intermolecular Coulomb energy.

The model systems chosen for this study are the three crystal structures acetylene, carbon dioxide, and cyanogen. The relevant crystal data are given in Table 1. The molecules chosen have appreciable quadrupole moments but are non-polar and occupy crystallographic inversion centers. Accordingly, while the electrostatic part of the lattice energies is far from negligible, the induced molecular polarization is likely to be unimportant. This means that we can safely treat the

Table 1. *Crystal data of acetylene (high-temperature form), carbon dioxide, and cyanogen*

| Compound | Space group | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | <i>T</i> (K) | Reference |
|-------------------------------|-------------|--------------|--------------|--------------|--------------|-----------|
| C ₂ H ₂ | <i>Pa</i> 3 | 6.091 | | | 141 | (a) |
| CO ₂ | <i>Pa</i> 3 | 5.54 | | | 0 | (b) |
| C ₂ N ₂ | <i>Pcab</i> | 6.31 | 7.08 | 6.19 | 178 | (c) |

References: (a) van Nes (1977), (b) Keesom & Köhler (1934), (c) Parks & Hughes (1963).

molecular charge densities as frozen in the evaluation of their mutual electrostatic interactions.

The molecular charge densities have been derived from the Hartree–Fock wavefunctions of McLean & Yoshimine (1967). The absolute accuracy of the Hartree–Fock charge-density maps is here of secondary import; more relevant to the present comparison is that such theoretical maps are far more detailed than any that are available experimentally. These calculated charge densities have been represented, for the purpose of the electrostatic calculations, at three levels of approximation.

Atomic moments (AM)

In the most detailed representation, the molecular charge density is decomposed into atomic fragments according to the stockholder recipe of Hirshfeld (1977). Each atomic fragment is then represented by its calculated net charge, dipole and quadrupole moments localized at the atomic nucleus.

Atomic charges (AC)

At an intermediate level of approximation each atom is represented by a point charge at its center, the values of the atomic charges being chosen to reproduce the calculated molecular quadrupole moment.

Molecular moment (MM)

The crudest approximation is to replace each molecule by a point quadrupole placed at its center of symmetry.

Table 2. *Input parameters for electrostatic calculations*

Atomic charges q (e), dipole moments μ (D), and quadrupole moments Θ (Buckingham) are according to Table 1 of Hirshfeld (1977). Effective charges q' (e) are chosen to reproduce calculated molecular quadrupole moments Θ^{mol} . All moments are directed along molecular axis, with positive sense to the right. Indicated bond lengths (Å) correspond to molecular dimensions adopted for the Hartree–Fock wavefunctions of McLean & Yoshimine (1967). [1 e = 1.6022×10^{-19} C; 1 D = 3.336×10^{-30} C m; 1 Buckingham = 3.336×10^{-40} C m².]

| | | | | | | | |
|-------------------------------|--------|-------|--------|--------|--------|-------|--------|
| C ₂ H ₂ | H | 1.059 | C | 1.207 | C | 1.059 | H |
| q | +0.094 | | −0.094 | | −0.094 | | +0.094 |
| μ | −0.494 | | −0.764 | | +0.764 | | +0.494 |
| Θ | +0.030 | | −0.083 | | −0.083 | | +0.030 |
| q' | +0.312 | | −0.312 | | −0.312 | | +0.312 |
| Θ^{mol} | | | | +7.188 | | | |
| CO ₂ | O | 1.136 | C | 1.136 | O | | |
| q | −0.207 | | +0.414 | | −0.207 | | |
| μ | +0.206 | | 0 | | −0.206 | | |
| Θ | −0.032 | | −1.594 | | −0.032 | | |
| q' | −0.410 | | +0.820 | | −0.410 | | |
| Θ^{mol} | | | −5.293 | | | | |
| C ₂ N ₂ | N | 1.157 | C | 1.380 | C | 1.157 | N |
| q | −0.126 | | +0.126 | | +0.126 | | −0.126 |
| μ | +0.158 | | +0.685 | | −0.685 | | −0.158 |
| Θ | −0.491 | | −0.738 | | −0.738 | | −0.491 |
| q' | −0.322 | | +0.322 | | +0.322 | | −0.322 |
| Θ^{mol} | | | | −9.069 | | | |

The parameter values appropriate to these models are listed in Table 2. For consistency the same value of the molecular quadrupole moment has been adopted for all three models. We note that in all three molecules the effective atomic charges q' required to reproduce this calculated value of Θ^{mol} are some two to three times larger than the directly evaluated charges q , *i.e.* these charges have been scaled up to compensate for the neglected atomic dipole and quadrupole moments.

The van der Waals part of the lattice energy was calculated from the atom–atom potentials advocated by Mirsky (1978). These have the form and the parameter values given in Table 3. They have been tested on a variety of crystal calculations and appear to be among the most suitable to be found in the literature. The H...H, C...C, and H...C potentials were derived from a selection of hydrocarbon crystal data and give good agreement with their observed structures, elastic constants, and sublimation energies (Mirsky, 1976). It should, however, be noted that these comparisons neglected the electrostatic contribution to the lattice energy so it is not quite correct to regard the derived potentials as representing the van der Waals energy alone. The N...N potential was deduced from the crystal data for N₂O, whose measured sublimation energy was explicitly corrected for the estimated quadrupole–quadrupole interaction energy (Mirskaya & Nauchitel', 1972). For the O...O potential a similar fit was made to the lattice energy of CO₂, corrected for the estimated electrostatic contribution (Kitaigorodskii, Mirskaya & Nauchitel', 1970). In all cases the potential between two unlike atoms has been derived according to the combining rules given by Mirskaya (1973).

At low temperature acetylene is orthorhombic, space group *Acam*, but accurate cell dimensions and atomic coordinates have been reported only for the deuterated compound (Koski & Sándor, 1975). Above 133 K it is cubic, *Pa3* (see Table 1), and it is this more symmetric structure that we have adopted for our present calculations. Table 4 lists the calculated van der Waals and electrostatic energies for molecule pairs occurring in this structure. The convergence of the corresponding calculated lattice energy is depicted in Fig. 1. The electrostatic term has been evaluated in accordance with each of the three models described above. Of

Table 3. *Atom–atom van der Waals potentials*
[$\varphi = -Ar^{-6} + B \exp(-ar)$]

| Atom pair | A (kJ mol ⁻¹ Å ⁶) | B ($\times 10^{-5}$) (kJ mol ⁻¹) | α (Å ⁻¹) |
|-----------|---|---|--------------------------------|
| C...C | 1761 | 3.00 | 3.68 |
| H...H | 121 | 0.21 | 4.29 |
| O...O | 1085 | 3.25 | 4.18 |
| N...N | 1084 | 1.76 | 3.78 |
| H...C | 494 | 0.78 | 3.94 |
| O...C | 1420 | 3.17 | 3.91 |
| N...C | 1387 | 2.31 | 3.73 |

particular interest is the observation that each molecule in this structure has binding interactions with all its near neighbors out to the fifth shell. Inspection of Fig. 1 shows that the calculated lattice energy has effectively converged at a limiting intermolecular separation of about 15 Å. The van der Waals and electrostatic terms make comparable contributions to the lattice energy. Comparison of the three electrostatic models shows a pattern that is typical for all three structures examined: the differences among these models quickly become negligible beyond the first one or two shells, but for the nearest neighbors models AC and MM give interaction energies 9 and 63% larger, respectively, than that obtained from the most detailed AM model. The electrostatic part of the lattice energy for the three models is -15.0 (AM), -16.1 (AC), and -23.0 (MM) kJ mol^{-1} .

Fig. 2 shows the calculated lattice energy of acetylene as a function of the unit-cell edge a , the molecular dimensions (Table 2) and orientation being held constant as a is varied. The electrostatic term has

Table 4. C_2H_2 : calculated van der Waals (u_{vdw}) and electrostatic (u_{el}) intermolecular energies (kJ mol^{-1} of dimer) for inner 12 shells around the reference molecule at 000

R is the center-to-center distance, and M is the number of equivalent molecules in the shell.

| Site | R (Å) | M | u_{vdw} | $u_{\text{el}}^{\text{AM}}$ | $u_{\text{el}}^{\text{AC}}$ | $u_{\text{el}}^{\text{MM}}$ |
|---------------------------|---------|-----|------------------|-----------------------------|-----------------------------|-----------------------------|
| $\frac{1}{2}\frac{1}{2}0$ | 4.306 | 12 | -1.656 | -2.034 | -2.212 | -3.326 |
| 100 | 6.091 | 6 | -0.267 | -0.589 | -0.634 | -0.867 |
| $1\frac{1}{2}1$ | 7.461 | 24 | -0.094 | -0.077 | -0.070 | -0.038 |
| 110 | 8.613 | 12 | -0.038 | -0.113 | -0.106 | -0.071 |
| $\frac{1}{2}10$ | 9.630 | 24 | -0.016 | -0.039 | -0.039 | -0.039 |
| 111 | 10.550 | 8 | -0.012 | +0.171 | +0.166 | +0.143 |
| $\frac{3}{2}1\frac{1}{2}$ | 11.396 | 48 | -0.006 | +0.033 | +0.033 | +0.032 |
| 200 | 12.182 | 6 | -0.004 | -0.025 | -0.026 | -0.027 |
| $2\frac{1}{2}1$ | 12.919 | 24 | -0.003 | +0.002 | +0.002 | +0.003 |
| $\frac{3}{2}0$ | 12.919 | 12 | -0.003 | -0.013 | -0.013 | -0.014 |
| 210 | 13.619 | 24 | -0.002 | -0.013 | -0.013 | -0.012 |
| $\frac{3}{2}1$ | 14.283 | 24 | -0.002 | -0.014 | -0.014 | -0.014 |

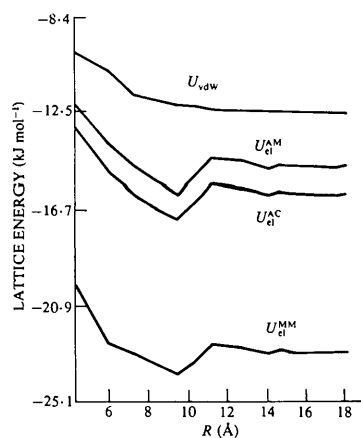


Fig. 1. C_2H_2 : components U_{vdw} and U_{el} , for three models, of calculated lattice energy vs limiting radius R .

been evaluated according to model AM and the calculation embraces 21 shells of neighbors, corresponding to a limiting radius of 18.3 Å at the experimental cell edge $a = 6.09$ Å. The van der Waals potential alone is seen to provide about 13 kJ mol^{-1} of lattice energy, compared to an experimental value of 24.3 kJ mol^{-1} (Table 5). This experimental determination is highly uncertain, depending on a doubtful extrapolation to 0 K of the sublimation energy measured in the high-temperature phase at 162 K. Adding the electrostatic term produces an overcorrection of the calculated lattice energy and shifts its minimum from 5.92 Å to a predicted cell dimension of 5.65 Å. The difference between this and the observed 6.09 Å is too large to be plausibly attributed to thermal expansion between 0 K and the experimental temperature of 141 K. Much of the discrepancy, in lattice energy and in cell edge, may arise from a grossly overestimated theoretical quadrupole moment, 7.19 Buckingham's compared to an experimental value of 3.0 (Stogryn & Stogryn, 1966). But an additional possibility is that the empirical atom-atom potentials we have employed may already include, in disguised form, a non-negligible fraction of the electrostatic contribution to the lattice energy.

Table 5. Experimental and calculated lattice energies (kJ mol^{-1})

The measured sublimation energy ΔH_s^T at temperature T is adjusted to 0 K by the approximate expression: $\Delta H_s^0 = \Delta H_s^T + 2RT$ (Rae & Mason, 1968). U_{exp} is the calculated lattice energy at the experimental cell dimensions; U_{min} is the minimum of U vs cell size.

| Crystal | ΔH_s^T | T (K) | ΔH_s^0 | Reference | $-U_{\text{exp}}$ | $-U_{\text{min}}$ |
|------------------------|----------------|---------|----------------|-----------|-------------------|-------------------|
| C_2H_2 | 21.8 | 162 | 24.3 | (a) | 27.6 | 31.6 |
| CO_2 | | | 26.9 | (b) | 32.0 | 32.0 |
| C_2N_2 | 32.4 | 224 | 36.2 | (c) | 30.3 | 30.5 |

References: (a) Jones (1960), (b) Pople (1954), (c) Perry & Bardwell (1925).

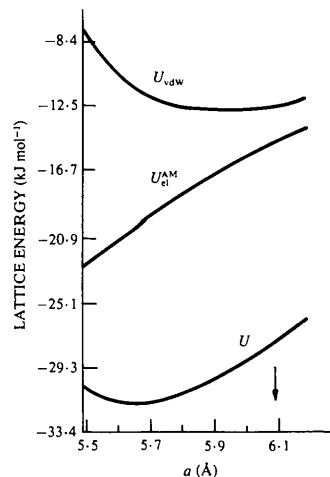


Fig. 2. C_2H_2 : variation of calculated lattice energy $U = U_{\text{vdw}} + U_{\text{el}}$ with unit-cell edge a . The arrow marks the observed value of a .

A corresponding series of calculations has been performed for CO_2 . Here, too, the three electrostatic models give roughly similar energies and the largest disparity among them is for the nearest-neighbor interactions, where the electrostatic energy is calculated as -2.4 (AM), -2.3 (AC), or -2.9 (MM) kJ mol^{-1} of dimer. Fig. 3 plots the lattice-energy contributions as a function of unit-cell edge. The van der Waals term alone is seen to be much smaller in magnitude than the experimental lattice energy (Table 5) and to reach a minimum at a much larger value of a than is found experimentally. Inclusion of the electrostatic energy improves the fit considerably, giving a calculated lattice energy of -32.0 kJ mol^{-1} (exp. -26.9) at $a = 5.51$ Å (exp. 5.54). This agreement is largely tautological, however, as the $\text{O}\cdots\text{O}$ van der Waals potential was originally derived (see above) to fit the crystal data for CO_2 with explicit allowance for the electrostatic contribution. Since this contribution had been evaluated from the experimental quadrupole moment of 4.3 Buckingham (Stogryn & Stogryn, 1966) it is entirely understandable that the theoretical value of 5.29 Buckingham appears to produce too large a correction.

Our final, and most revealing, example is cyanogen, space group $Pcab$. Here each molecule has three dif-

Table 6. C_2N_2 : calculated intermolecular energies (kJ mol^{-1} of dimer) for innermost shells

| Site | R (Å) | M | u_{vdw} | $u_{\text{el}}^{\text{AM}}$ | $u_{\text{el}}^{\text{AC}}$ | $u_{\text{el}}^{\text{MM}}$ |
|---------------------------|---------|-----|------------------|-----------------------------|-----------------------------|-----------------------------|
| $\frac{1}{2}0\frac{1}{2}$ | 4.420 | 4 | -1.983 | -2.982 | -3.825 | -7.071 |
| $0\frac{1}{2}0$ | 4.702 | 4 | -1.209 | -4.354 | -4.586 | -5.271 |
| $\frac{1}{2}\frac{1}{2}0$ | 4.742 | 4 | -1.894 | +1.223 | +1.327 | +1.625 |
| 001 | 6.190 | 2 | -0.965 | -1.402 | -1.278 | -0.631 |
| 100 | 6.310 | 2 | -0.322 | +0.308 | +0.306 | +0.212 |
| 010 | 7.080 | 2 | -0.200 | -0.243 | -0.293 | -0.479 |
| $\frac{1}{2}\frac{1}{2}1$ | 7.798 | 8 | -0.208 | -0.126 | -0.096 | -0.025 |
| $1\frac{1}{2}\frac{1}{2}$ | 7.869 | 8 | -0.122 | -0.066 | -0.074 | -0.097 |
| $\frac{1}{2}1\frac{1}{2}$ | 8.346 | 8 | -0.105 | -0.258 | -0.248 | -0.206 |

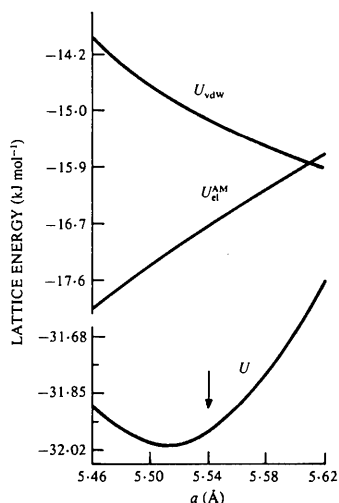


Fig. 3. CO_2 : variation of calculated lattice energy with unit-cell edge a . The arrow marks the observed value of a . Note expanded scale for total U .

ferent sets of nearest and of next-nearest neighbors, etc., at appreciably different distances and mutual orientations. Table 6 lists the calculated intermolecular energies for the first few such shells, where the differences among the three electrostatic models are, as usual, most pronounced. For all these models the calculated lattice energy again converges within a limiting radius of 15 Å. The van der Waals part of the calculated lattice energy is -14.5 kJ mol^{-1} , while the electrostatic term, for the several models, contributes -15.7 (AM), -17.2 (AC), or -23.6 kJ mol^{-1} (MM).

Fig. 4 (full curves) shows the variation of the calculated lattice energy, and of its van der Waals and electrostatic components, as the unit cell is expanded or contracted uniformly in all three axes. As in CO_2 the inclusion of the electrostatic term greatly improves the calculated values of the cell dimensions and of the total lattice energy (Table 5). This result is a more convincing demonstration of the essential validity of the model, since the cyanogen crystal played no role in the derivation of the $\text{N}\cdots\text{N}$ van der Waals potential.

Further vindication of the model would be a demonstration that it can explain the difference in space group between CO_2 and C_2N_2 . To show that space group $Pa3$ provides the most stable structure for CO_2 would require an exhaustive search for minimum-energy structures in all possible subgroups of $Pa3$. The converse is much more readily tested, that a $Pa3$ structure for C_2N_2 leads to a higher calculated energy than the observed $Pcab$ structure. This comparison is shown in Fig. 4, which plots the calculated energies of the two alternative cyanogen structures. Corresponding points on the two sets of curves in this figure

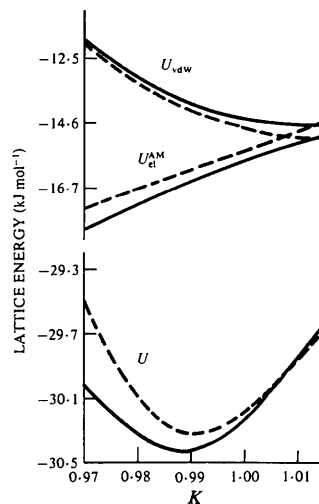


Fig. 4. C_2N_2 : variation of calculated lattice energy with uniform expansion or contraction of unit cell; scale factor K multiplies observed unit-cell edges. Full lines - observed $Pcab$ structure; broken lines - hypothetical $Pa3$ structure having the same unit-cell volume.

refer to equal unit-cell volumes. Throughout the region of interest the orthorhombic structure is seen to be uniformly more stable than the corresponding cubic structure. This is not the case, however, for the van der Waals energy alone, which is higher in the orthorhombic than in the cubic structure. Thus inclusion of the electrostatic contribution is apparently necessary to explain the preference of cyanogen for space group $Pcab$ rather than $Pa3$. The reverse order found for the van der Waals energy may seem incongruous inasmuch as the minimum-energy structure in the subgroup symmetry $Pcab$ cannot possibly be less stable than the more symmetric $Pa3$ structure. But we have not, in fact, sought the most stable $Pcab$ structure. The orthorhombic structure plotted in Fig. 4 is simply the observed structure, with unit-cell shape and molecular orientation fixed, the only variable parameter being a single factor scaling all three cell edges. This is directly comparable to the single variable cell edge in the cubic $Pa3$ structure. Thus it is not entirely trivial that the observed orthorhombic structure for cyanogen gives a lower calculated energy than the alternative cubic structure.

A more searching test of the potential function would be to vary all structural parameters, *i.e.* cell dimensions and molecular orientation, in search of a global energy minimum for comparison with the observed crystal structure of cyanogen. But this is a lengthy and expensive task, while a partial search, in one or two dimensions only, is of doubtful value. For example, as has been repeatedly demonstrated, rotation of the molecule about one or two axes is virtually certain to produce a sharp energy minimum near the observed orientation unless the cell dimensions are simultaneously allowed to vary from their experimental values.

The results reported above indicate that the calculation of crystal lattice energies can be significantly improved by the explicit inclusion of the electrostatic energy. This can evidently be approximated reasonably well by a fairly crude representation of the molecular charge distribution. Representing each molecule by a point dipole (untested) and quadrupole appears to be unsatisfactory even for the small molecules examined here. But a point charge at each atomic center yields electrostatic lattice energies within about 10% of those obtained from a much more detailed description of the charge density, even though the discrepancy for individual molecular pairs may be close to 30% as seen in Table 6. The adequacy of such a point-charge model should not change drastically with the size of the molecule. Accordingly, it seems that efforts to improve on the usual atom-atom approximation might usefully be directed towards the derivation of appropriate values of effective point charges for incorporation in a model of this type.

Note, however, that the simplicity of the atomic-charge model described above owes much to the

unusually high symmetry of the three molecules studied. In the absence of any simplifying symmetry, representing the molecular Coulomb field up to quadrupole terms requires us to fit one monopole, three dipole, and five independent quadrupole components. Clearly, this cannot be done with three or four charges at predetermined positions. Achieving an adequate representation by point charges may, in the general case, require placing such charges at other than the atomic centers.

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