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Electron-density-based calculations of intermolecular energy: case of urea

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Abstract

The intermolecular interaction energy in crystalline urea has been calculated both from diffraction data and from the Hartree–Fock crystalline electron-density distribution, using a modified atom–atom approximation scheme. The electrostatic part of this energy has been calculated from the atomic multipole moments, obtained by adjustment of the multipole model to experimental X-ray and to theoretical Hartree–Fock structure amplitudes. To obtain the induction energy, multipole moments were calculated from structure amplitudes for the crystalline electron density and from those that refer to the electron density of a superposition of isolated molecules. This worked well for the calculation of the interaction energy from Hartree–Fock data (6% difference from the sublimation-energy value), but not for the interaction energy from experimental data, where the moments of the superposition have to come from Hartree–Fock calculations: the two sets of multipole moments are far too different. The uncertainty of the phases of the structure amplitudes, combined with systematic errors in the theoretical data and noise in the experimental values, may account for the discrepancies. The nature of the different contributions to intermolecular interactions for urea is examined.

1. Introduction

The investigation of the structural behaviour of molecules in a crystal often requires an estimate of the energy of the intermolecular interaction. There are many methods to solve this problem, which have been reviewed many times (Pullman, 1978; Kaplan, 1985; Pertsin & Kitaigorodsky, 1986; Tsirelson & Ozerov, 1996). A majority of them is based on empirical or semi-empirical atom–atom potential schemes because a rigorous quantum-chemical study of the system is difficult. The various atom–atom potentials contain terms that more or less correspond to certain types of interaction. Each of these terms contains one or more parameters that are determined by fitting the total interaction energy to experimental values. Since many parameters are fitted at the same time to a limited set of experimental data, not much physical importance can be assigned to the individual terms. This makes the transfer of terms from one scheme to another a risky business. It is evident, however, that the more the model incorporates 'first principles' in the sense that individual terms carry physical meaning, the more transferability becomes valid.

In the atom–atom approximation (Kaplan, 1985; Tsirelson & Ozerov, 1996), the interaction energy is usually represented by a sum of Lennard-Jones and electrostatic terms. The physical meaning assigned to each of these terms and the way in which they are calculated in the various schemes differs considerably. The approach, which was outlined by Berkovitch-Yellin & Leizerowitz (1980, 1982) and Tsirelson *et al.* (1982) and developed by Spackman (1986*a*,*b*, 1987, 1992) and Spackman *et al.* (1988), is, in our opinion, attractive since it is based on a few well defined approximations only. The total interaction energy, $E_{\rm intermol}$, is written as

$$E_{\rm intermol} = E_{\rm rep} + E_{\rm disp} + \varepsilon_{\rm es}, \quad (1)$$

where the first two Lennard-Jones terms, describing the short-range repulsive and the long-range attractive energy, respectively, are written in the traditional atom–atom form:

$$E_{\rm rep} = \sum_{i<j} b_i b_j \exp[-(c_i + c_j) r_{i,j}], \qquad E_{\rm disp} = -\sum_{i<j} a_i a_j r_{i,j}^{-6}. \quad (2)$$

The $\varepsilon_{\rm es}$ term arises from the classical electrostatic interaction energy between the charge distributions of the molecules in the crystal. Spackman (1986*a*) calculated the parameters a_i from atomic C_6 dispersion coefficients and b_i, c_i *via* the electron-gas theory within the Kim & Gordon (1974) approximation. To obtain an expression for $\varepsilon_{\rm es}$, Spackman (1986*b*) considered the total charge density in the crystal unit cell, σ, as the sum of pseudo-atomic nonspherical charge densities, $\sigma^{\rm at}$, the latter being the sum of a spherical atomic term (nuclei included), $\sigma^{\rm at}_{\rm sph}$, and a deformation-electron-density (ED) term, $\delta\rho^{\rm at}$:

$$\sigma^{\rm at} = \sigma^{\rm at}_{\rm sph} + \delta\rho^{\rm at} \tag{3}$$

In the expression for the electrostatic interaction between the pseudo-atoms A and B, the following product is encountered:

$$\sigma^{\rm at}_{A}\sigma^{\rm at}_{B} = \sigma^{\rm at}_{A,{\rm sph}}\sigma^{\rm at}_{B,{\rm sph}} + \sigma^{\rm at}_{A,{\rm shp}}\delta\rho^{\rm at}_{B} + \sigma^{\rm at}_{B,{\rm shp}}\delta\rho^{\rm at}_{A} + \delta\rho^{\rm at}_{A}\delta\rho^{\rm at}_{B}. \tag{4}$$

The first term in this expansion is found in the expression for the classical electrostatic interaction energy between two spherical atomic charge distributions. Kim & Gordon (1974) included this term in $E_{\rm rep}$. The remaining terms yield $E_{\rm es}$ and $E_{\rm pen}$ defined by

$$E_{\rm es} = -\sum_{A<B}\sum \iint \delta\rho^{\rm at}_{A}\delta\rho^{\rm at}_{B}|r_A - r_B|^{-1}\,{\rm d}r_A\,{\rm d}r_B, \tag{5}$$

$$\begin{aligned} E_{\rm pen} = -\sum_{A<B}\sum \iint &(\sigma^{\rm at}_{A,{\rm sph}}\delta\rho^{\rm at}_{B} + \sigma^{\rm at}_{B,{\rm sph}}\delta\rho^{\rm at}_{A}) \\ &\times |r_A - r_B|^{-1}\,{\rm d}r_A\,{\rm d}r_B. \end{aligned} \tag{6}$$

$E_{\rm es}$ describes the interaction between the atomic deformation ED distributions; it is, as we will see below, the predominant term in the intermolecular energy. $E_{\rm pen}$ describes the interaction between the deformation atomic ED on the one atom with the spherical charge density distribution on the other.

Spackman (1986*b*) assumed the interacting molecules to be unpolarized. This allowed him to derive their charge distribution from the charge distribution in the crystal by applying some partitioning scheme. However, the intermolecular interactions result in the deformation of the molecular charge distribution due to mutual polarization and to compression due to exchange repulsion. For an individual *free* molecule, such a redistribution of the electron density means an increase of energy, an increase that is more than recovered when the molecule is placed in the crystal. Consequently, the expressions for the electrostatic energy arising from permanent and from induced ED distributions appear differently, and it is necessary to separate the total ED in induction and permanent parts. The assumption of unpolarized molecules implies the neglect of this increase in energy. A more quantitative discussion of this problem is found in Appendix A.

The practical calculation of $E_{\rm intermol}$ requires some additional approximations. The first of them is the replacement of the continuous atomic charge distributions by atom-centred multipole moments in the expressions for the electrostatic interaction and the replacement of integrals over these distributions by summations over these moments. The second one is the description of the energy of the hydrogen bond. The latter in Spackman's approach is taken into account by omitting $E_{\rm rep}$ and $E_{\rm disp}$ terms for proton–acceptor interaction. This is based on the Buckingham & Fowler (1983) suggestion that the hard-sphere radius for the H atom can be taken as zero.

In the present paper, we will describe the calculation of intermolecular interaction energy in crystalline urea using the outlined electron-density-based approach.

2. Computation

To calculate the $E_{\rm rep}$ and $E_{\rm disp}$ terms, we have used the parameters listed by Spackman (1986*a*). The energy of hydrogen bonds was calculated within the Buckingham & Fowler (1983) approximation. The calculation of the $E_{\rm es}$ and $E_{\rm pen}$ terms was based on the structure amplitudes from a recent accurate X-ray diffraction study at 148 K of urea by Zavodnik *et al.* (1999) as well as from the Hartree–Fock 6-21G** calculation of crystalline urea by Dovesi *et al.* (1990). The ED of urea was described by the multipole model of Hansen & Coppens (1978) and adjusted to the structure amplitudes using program *MOLDOS*96 (Protas, 1996). Atomic multipole functions in the study of Zavodnik *et al.* (1999) were extended up to the hexadecapole level on the C atom, up to octopoles on the N and O atoms, and up to dipoles on H atoms. To take into account the intermolecular interaction energy in more detail, we have introduced additionally the hexadecapole term for the O atom and have performed a new refinement of this modified multipole model. The extinction and thermal atomic parameters for experimental data as well as exponential parameters were taken from Zavodnik *et. al.* (1999) and were not refined. The refinement process over reflections with $\sin\theta/\lambda \leq 0.9$ Å^{-1} was stable (experiment: $R = 0.013$, $R_w = 0.019$, $S = 1.75$; theory: $R = 0.014$) with the highest correlation coefficients being 0.908 for κ_2 and $Ozzz$ of the C atom for experimental structure amplitudes, and 0.892 for the first monopoles on the N and the H2 atoms for quantum-chemical-calculated ones. The results of the multipole model refinements have been deposited.†

To calculate the $E_{\rm es}$, we have used the expression obtained by Buckingham (1978), and adopted by Moss & Feil (1981), who presented it in a form of individual multipole–multipole terms up to R^{-5}. In order to take into account all moment–moment terms describing the contributions to the electrostatic interaction energy up to R^{-6}, we have completed this list of expressions with dipole–hexadecapole and quadrupole–octopole terms. The values of traceless multipole moments for each atom contributing to the $E_{\rm es}$ were obtained using expressions

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† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV0013). Services for accessing these data are described at the back of the journal.

Table 1. *Traceless atomic mutipole moments for urea obtained from the experimental and theoretical structural amplitudes*

Atoms	C		O		N		H1		H2	
	Exp	Theory	Exp	Theory	Exp	Theory	Exp	Theory	Exp	Theory
Charge	−0.220 (170)	0.370 (120)	−0.180 (110)	−0.700 (60)	−0.130 (120)	−0.350 (110)	0.180 (60)	0.250 (40)	0.160 (50)	0.270 (40)
μ_x					0.002 (7)	0.007 (2)	−0.008 (8)	0.016 (6)	0.005 (6)	−0.006 (4)
μ_y					0.029 (6)	0.0620 (5)	−0.063 (7)	−0.076 (9)	−0.050 (9)	−0.070 (10)
μ_z	−0.100 (20)	0.240 (30)	0.080 (20)	0.005 (5)						
θ_{xx}	0.290 (20)	0.380 (20)	0.001 (8)	−0.001 (2)	−0.006 (7)	0.001 (2)				
θ_{yy}	−0.110 (50)	−0.240 (30)	−0.008 (6)	−0.008 (2)	−0.001 (6)	0.005 (1)				
θ_{zz}	−0.190 (20)	−0.140 (10)	0.007 (4)	0.009 (1)	0.007 (4)	−0.007 (1)				
θ_{xy}					−0.002 (3)	−0.002 (1)				
Ω_{xxx}					−0.016 (7)	0.002 (2)				
Ω_{yyy}					0.090 (10)	0.011 (1)				
Ω_{zzz}	−1.010 (20)	−1.050 (40)	−0.004 (6)	−0.008 (2)						
Ω_{xxy}					−0.070 (10)	−0.008 (1)				
Ω_{xyy}					0.002 (5)	0.001 (1)				
Ω_{xzz}					0.013 (5)	−0.003 (1)				
Ω_{yzz}					−0.016 (5)	−0.002 (1)				
Ω_{xxz}	0.100 (2)	−0.100 (10)	−0.029 (8)	0.005 (1)						
Ω_{yyz}	0.920 (20)	1.180 (20)	0.032 (7)	0.003 (1)						
H_{xxxx}	−0.500 (30)	0.200 (40)	−0.030 (10)	−0.004 (1)						
H_{xxyy}	0.370 (70)	−0.200 (100)	−0.001 (1)	−0.001 (1)						
H_{xxzz}	0.100 (30)	−0.100 (30)	0.034 (30)	0.005 (1)						
H_{yyyy}	0.200 (400)	1.100 (200)	0.010 (20)	−0.002 (2)						
H_{yyzz}	−0.500 (20)	−1.000 (10)	−0.010 (10)	0.003 (1)						
H_{zzzz}	0.500 (100)	1.060 (90)	−0.024 (5)	−0.008 (3)						

Table 2. *Calculated contributions in the molecular interaction energy $E_{intermol}$ (1) and comparison with experimental sublimation energy (kJ mol^{-1}): E_{es} was calculated with theoretical structure amplitudes*

E_{es}	$E_{\mathrm{es}}^{\mathrm{perm}}$	E_{ind}	E_{pen}	E_{rep}	E_{disp}	E_{intermol}	H_{subl}^{298}
−111 (7)	−96 (5)	−8 (5)	−2	71	−55	−90 (9)	96

Table 3. *Energies of pair interaction of urea molecule N1 (see Fig. 1) with neighbouring molecules (kJ mol^{-1})*

Number and position of the neighbouring molecule	E_{es}	$E_{\text{es}}^{\text{perm}}$	E_{ind}	U†	$E_{\text{mol-mol}}$‡
N2 $(X, Y, 1+Z)$	−64.4	−55.3	−4.6	3.4	−56.4
N3 $(Y, -X, 1-Z)$	−36.9	−33.3	−1.8	3.7	−31.4
N4 $(X, Y, 2+Z)$	−5.1	−4.0	−0.6	−0.1	−4.6
N5 $(X, 1+Y, Z)$	6.0	4.4	0.8	−1.7	3.5
N6 $(1+X, 1+Y, Z)$	3.1	2.4	0.4	−0.2	2.5
N7 $(X-1, 1+Y, Z)$	4.1	3.2	0.5	−0.4	3.2
N8 $(Y, -X, 2-Z)$	5.0	3.8	0.6	−0.3	4.1
N9 $(Y, -X, -Z)$	2.7	3.6	−0.5	6.1	9.3
N10 $(1+X, Y, 1+Z)$	0.0	0.1	−0.05	−0.4	−0.35

† $U = E_{\text{rep}} + E_{\text{disp}} + E_{\text{pen}}$. ‡ $E_{\text{mol-mol}} = E_{\text{es}}^{\text{perm}} + E_{\text{ind}} + U$.

$$\mu_\alpha^{\text{at}} = -\int_V \delta\rho^{\text{at}} r_\alpha \, \mathrm{d}V, \qquad (7)$$

$$\theta_{\alpha\beta}^{\text{at}} = -\tfrac{1}{2}\int_V \delta\rho^{\text{at}} [3r_\alpha r_\beta - r^2\delta_{\alpha\beta}] \, \mathrm{d}V \qquad (8)$$

$$\Omega_{\alpha\beta\gamma}^{\text{at}} = -\tfrac{1}{2}\int_V \delta\rho^{\text{at}} [5r_\alpha r_\beta r_\gamma - r^2(r_\alpha\delta_{\beta\gamma} + r_\beta\delta_{\alpha\gamma} + r_\gamma\delta_{\alpha\beta})] \, \mathrm{d}V \qquad (9)$$

$$H_{\alpha\beta\gamma\eta}^{\text{at}} = -\tfrac{1}{8}\int_V \delta\rho^{\text{at}} [35r_\alpha r_\beta r_\gamma r_\eta - 5r^2(r_\beta r_\gamma\delta_{\alpha\eta} + r_\alpha r_\gamma\delta_{\beta\eta} + r_\alpha r_\beta\delta_{\gamma\eta} + r_\alpha r_\eta\delta_{\beta\gamma} + r_\beta r_\eta\delta_{\alpha\gamma} + r_\gamma r_\eta\delta_{\alpha\beta}) + r^4(\delta_{\alpha\eta}\delta_{\beta\gamma} + \delta_{\alpha\gamma}\delta_{\beta\eta} + \delta_{\alpha\beta}\delta_{\gamma\eta})] \, \mathrm{d}V. \qquad (10)$$

Here, α, β, γ, $\eta = x, y, z$, and $\delta\rho^{\text{at}}$ is the nonspherical part of the atomic ED presented as multipole expansion over real spherical harmonic functions, y_{lm}, up to fourth order according to Hansen & Coppens (1978):

$$\rho^{\text{at}}(r) = \sum_{l=1}^{4} \kappa''^3 R_l(\kappa'' r) \sum_{m=-l}^{l} P_{lm} y_{lm}(\mathbf{r}/r). \qquad (11)$$

The values of moments obtained are listed in Table 1.

As was stated above, to calculate the E_{es} term from the ED of a three-dimensional periodic crystal, it is necessary to separate the total redistribution of the ED in permanent and induction parts:

$$\delta\rho = \delta\rho_{\text{perm}} + \delta\rho_{\text{ind}}. \qquad (12)$$

The $\delta\rho_{\text{perm}}$ describes the electron redistribution when atoms form isolated molecules, $\delta\rho_{\text{ind}}$ is the ED induced when isolated molecules form a crystal. We now write (see Appendix *A*)

$$E_{\text{es}} = E_{\text{es}}^{\text{perm}} + 2E_{\text{es}}^{\text{ind}}. \qquad (13)$$

The energy $E_{\text{es}}^{\text{perm}}$ related to $\delta\rho_{\text{perm}}$ is calculated by (5) using the superposition of nonperturbed isolated molecules with the experimental geometry; *i.e.* we suppose that the molecular geometry in a crystal is the same as the one in the gas phase. The ED for the molecular superposition was obtained from an *ab initio* Hartree–Fock 6-21G** calculation by Dovesi *et. al.* (1990).

To obtain E_{ind}, the calculation with (5) is repeated using the ED of a crystal. We have calculated the electrostatic energy both from refined experimental data and from an *ab initio* Hartree–Fock calculation of the molecules in a crystal. The difference between the results of the crystal and molecular superposition calculations is *twice* the induction energy $E_{\text{es}}^{\text{ind}}$. In all these calculations, the traceless atomic multipole moments from Table 1 were used.

The same moments were also used in the calculation of E_{pen} (6). The spherical atomic charge densities were derived from the analytical wave functions of Clementi & Roetti (1974).

3. Results and discussion

The results of the calculations are collected in Tables 1, 2 and 3. Inspection of Table 1 shows a large difference in the values of the charges on the C atom derived from the experimental and Hartree–Fock structure amplitudes; even their signs are different. Significantly higher negative charges are observed for the O and the N atoms in the case of the theoretical structure amplitudes. It results, in general, in different monopole–monopole contributions to the dipole moments.

With such a large difference in multipole moments between experiment and theory, we can hardly expect agreement in energy values. Table 2 shows that the interaction energy of urea obtained from theoretical multipole moments agrees quite well with the experimental value of the sublimation energy taken from De Wit *et al.* (1983). However, the electrostatic energy based on these crystal multipole moments, $E_{\text{es}} = -111\,(7)$ kJ mol^{-1}, differs considerably from the value obtained from the experimental data: $-68\,(15)$ kJ mol^{-1}, the monopole–monopole contribution is 3.4 times lower in the latter case. To complicate the situation, the atomic multipoles based on the experimental structure amplitudes yield a dipole moment of the molecules in the crystal of 4.2 (16) D, which is close to the experimental solid-state value of

4.65 D (Lefebvre, 1973), while the Hartree–Fock data result in a molecular dipole moment of 5.4 (8) D.

If, following Spackman (1986*b*), we neglect the $E_{\rm ind}$ for the case of the experimental structure amplitudes, we arrive at the value $E_{\rm intermol} = -54\,(15)$ kJ mol^{-1}, which is close to $E_{\rm intermol} = -66\,(24)$ kJ mol^{-1} obtained for urea by Spackman *et al.* (1988).

To estimate these results, note that the value of $E_{\rm es} = E^{\rm perm}_{\rm es} + 2E^{\rm ind}_{\rm es}$ should be more negative than $E^{\rm perm}_{\rm es}$ because the polarization (induction) energy is always negative. However, the $E_{\rm es}(\text{exp.}) = -68\,(15)$ kJ mol^{-1} is less negative than $E^{\rm perm}_{\rm es} = -96\,(5)$ kJ mol^{-1}. Hence it is impossible to obtain the induction energy by taking the difference between the energy calculated from experimental data and the energy derived by the same multipole refinement of Hartree–Fock structure amplitudes calculated for the superimposed molecules. Hence we shall focus in the remainder of this paper on the energy calculated with the present method from Hartree–Fock structure amplitudes. Calculated contributions in this energy are presented in Table 2.

The deformation ED's calculated using experimental and theoretical multipole parameters are very similar to those of Zavodnik *et al.* (1999). It seems that the small differences, however, have a rather large destabilizing effect on the partitioning of the total electron density, yielding quite different multipole moments. Since the energy calculations crucially depend on these moments, the method fails to yield interaction energies. All our attempts to improve the $E_{\rm es}$ value by changing the length of the multipole model and tactics of the refinement were unsuccessful.

It should be noted that urea is a noncentrosymmetric crystal and refinement of any structural model yields an uncertainty in the phases of the structure amplitudes, closely related to the noise in the experimental data. de Vries *et al.* (1999) showed recently that the resulting uncertainty in the ED of urea is of the same magnitude as the interaction densities. Consequently, it is impossible to derive $\delta\rho_{\rm ind}$ from the difference between the experimental ED, distorted by noise, and the ED calculated for isolated molecules. The same holds for $E_{\rm ind}$. The problem is aggravated by the systematic errors in the theoretically derived ED. Thus, the consistent calculation of $E_{\rm intermol}$ from a combination of experimental and theoretical data for a noncentrosymmetric crystal is questionable.

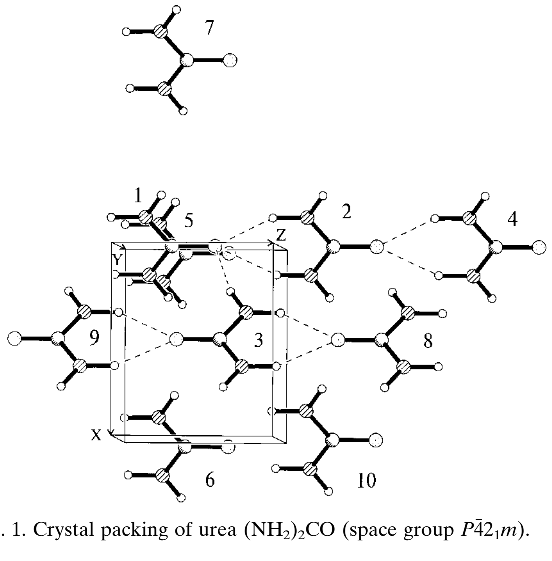

Fig. 1. Crystal packing of urea $(NH_2)_2CO$ (space group $P\bar{4}2_1m$).

Another remark concerns the way in which the hydrogen bond is treated. The Buckingham–Fowler approximation, which has been used in the present work, has, in our opinion, limited validity and additional study of this problem is needed. Analysis of early studies dealing with the problem of the hydrogen-bond description (Kuleshova, 1982; Kroon-Batenburg & Kanters, 1983; Filippini & Gavezzotti, 1994) suggests that the description of the H-bond interaction by modification of the $6-\exp$ (or $6-n$) atom–atom potentials might yield better results.

Our results based on the Hartree–Fock structure amplitudes allow us to examine the nature of interaction between molecules in the urea crystal. Calculated energies for pairs of nearest-neighbouring molecules in crystalline urea are listed in Table 3. Interaction energies of the central molecule $[(X, Y, Z)$ (^{1}1) in Fig. 1] with neighbouring ones $[(X, Y, 1+Z)$ (^{1}2) and $(Y, -X, 1-Z)$ (^{1}3)] dominate the total energy due to the large electrostatic contribution in the hydrogen bond in these pairs. The interaction energy of a dimer with two hydrogen bonds is about twice the energy of a dimer involving a single H-bond. The interaction between the other pairs is mostly repulsive. Most important is the repulsion between molecules $[(X, Y, Z)$ and $(Y, -X, -Z)$ (^{1}9)]. Crystallization of urea can be assumed to start by formation of H-bonded chains.

APPENDIX *A*
Electrostatic energy in crystals

The multipole moments of molecules in crystals differ from those of isolated molecules. This has consequences for the interaction energy defined as

$$E_{\rm intermol} = E_{\rm crystal} - \sum_A E^A_{\rm molecule}, \qquad (14)$$

in which $E^A_{\rm molecule}$ is the energy of the isolated molecule A. Hohenberg & Kohn's (1964) theorem, stating that there is a unique relation between the energy and the electron-density distribution makes it clear that any method that sets out to calculate the interaction energy from the ED requires the ED of both the crystal and the constituting molecules.

The electrostatic interaction energy E_{es} is defined as the work to be performed to move a molecule from infinity, where it can be considered to be isolated, to its site in the crystal against electrostatic forces due to the other molecules in the crystal. The electric field due to these molecules is inhomogeneous and its value in the region of the molecule under consideration can be expressed in a series of which we retain only the first two terms:

$$F_\mu(\mathbf{r}) = F^c_\mu + \sum_\nu r_\beta \big(\partial F_\mu/\partial r_\nu\big)_c. \tag{15}$$

$\mathbf{r}$ is the position vector with respect to the centre of gravity of the molecule, F^c_μ is the μ component of the electric field at this centre, $\mu, \nu = x, y, z$. The electrostatic force on the molecule is given by

$$\begin{aligned} K_\mu &= \int_{\text{vol}} \rho(\mathbf{r}) F_\mu(\mathbf{r})\, \mathrm{d}^3\mathbf{r} \\ &= \int_{\text{vol}} \rho(\mathbf{r})[F^c_\mu + \mathbf{r}\cdot\nabla F_\mu]\, \mathrm{d}^3\mathbf{r} \\ &= F^c_\mu \int_{\text{vol}} \rho(\mathbf{r})\, \mathrm{d}^3\mathbf{r} + \nabla F_\mu \int_{\text{vol}} \rho(\mathbf{r})\mathbf{r}\, \mathrm{d}^3\mathbf{r} \\ &= F^c_\mu Q + \nabla F_\mu \mathbf{d}, \end{aligned} \tag{16}$$

where the molecular charge $Q = \int_{\text{vol}} \rho(\mathbf{r})\, \mathrm{d}^3\mathbf{r}$ (nuclear charges can be easily taken into account) and the dipole moment $d = \int_{\text{vol}} \mathbf{r}\rho(\mathbf{r})\, \mathrm{d}^3\mathbf{r}$ are introduced. The dipole moment depends on the strength of the field F^c according to $\mathbf{d} = \mathbf{d}^0 + \alpha\mathbf{F}^c$.

If the molecule is moved from infinity to its site along the path s, the electrostatic energy is given by

$$\begin{aligned} E_{es} &= -\int_\infty^R \sum_\mu K_\mu\, \mathrm{d}s_\mu \\ &= -\int_\infty^R \sum_\mu (F^c_\mu Q + \mathbf{d}\nabla F_\mu)\, \mathrm{d}s_\mu \\ &= -Q \int_\infty^R \sum_\mu F^c_\mu\, \mathrm{d}s_\mu - \mathbf{d}^0 \int_\infty^R \sum_\mu \nabla F^c_\mu\, \mathrm{d}s_\mu \\ &\quad - \alpha \sum_\omega F^c_\nu \int_\infty^R \sum_\mu \nabla F^c_\mu\, \mathrm{d}s_\mu. \end{aligned} \tag{17}$$

The first term equals $Q\varphi$, in which φ is the electrostatic potential, the second one $-\mathbf{d}^0\cdot\mathbf{F}^c$, while the third one needs some rewriting. The use of

$$\partial F_\mu/\partial r_\nu = -\partial^2\varphi/r\partial r_\nu \partial r_\mu = \partial F_\nu/\partial r_\mu \tag{18}$$

gives

$$\begin{aligned} &-\int_\infty^R \sum_\mu \sum_\nu \alpha F^c_\nu (\partial F^c_\nu/\partial r_\mu)\, \mathrm{d}s_\mu \\ &\quad = -\int_\infty^R \sum_\mu \alpha F^c_\nu\, \mathrm{d}F^c_\nu = -\tfrac{1}{2}\alpha\mathbf{F}^c(R)\cdot\mathbf{F}^c(R). \end{aligned} \tag{19}$$

We can now re-write the electrostatic energy in the following way:

$$\begin{aligned} E_{es} &= Q\varphi - [\mathbf{d}^0 + \alpha\mathbf{F}^c(R)]\cdot\mathbf{F}^c(R) + \tfrac{1}{2}\alpha\mathbf{F}^c(R)\cdot\mathbf{F}^c(R) \\ &= Q\varphi - \mathbf{d}^0\cdot\mathbf{F}^c(R) - \tfrac{1}{2}\alpha\mathbf{F}^c(R)\cdot\mathbf{F}^c(R). \end{aligned} \tag{20}$$

The quantities that enter the first two terms can be obtained from the ground-state ED, but the third term requires the knowledge of the induced dipole moment, a quantity that can be derived from the difference between the ED's of the molecule in the crystal and the isolated molecule.

Similar discussions can be found in the works by Coulson & Eisenberg (1966) and by Berendsen *et al.* (1987).

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