

## Current version of the PIXEL theory

Deposited as APPENDIX I to: Non-conventional bonding between organic molecules.

### The "halogen bond" in crystalline systems

Angelo Gavezzotti, Mol. Phys. 2008, 106, 1473-1485.

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### Coulombic energies

Consider a molecule (A) with nuclei of charge  $Z_j$  at points  $(j) = [x_j y_j z_j]$ . Let  $\rho_k$  be the electron density in an elementary volume  $V_k$  centered at point  $(k) = [x_k y_k z_k]$ .  $\rho_k$  is derived from MP2/6-31G\*\* wavefunctions. Each e-pixel has charge  $q_k = \rho_k V_k$ . In an usual MO calculation for a medium size organic molecule, with typical steps of 0.08 Å, one has some  $10^6$  pixels, too many for practical use; the distribution is then contracted into  $n \times n \times n$  super-pixels,  $n$  being called the condensation level. Each pixel is assigned to a particular atom in the molecule, as follows. Let  $p$  be the number of atoms for which the nucleus-pixel distance is smaller than the atomic radius. If  $p=1$ , the pixel is assigned to that atom. If  $p > 1$ , the pixel is assigned to the atom from which the distance is the smallest fraction of the atomic radius. If  $p = 0$ , the pixel is assigned to the atom whose atomic surface is nearest.

Consider now a second molecule, B with nuclei of charge  $Z_m$  at points  $(m) = [x_m y_m z_m]$ , and whose e-pixels of charge  $q_i = \rho_i V_i$  are at positions  $(i) = [x_i y_i z_i]$ . Let  $R_{ln}$  be the distance between any two centers of pixels or nuclear positions  $l$  and  $n$ ; the electrostatic potential  $\Phi_i$  generated by molecule A at point (i) of the charge density of molecule B and that generated by molecule A at nucleus  $m$  of molecule B,  $\Phi_m$ , with the corresponding Coulombic potential energies  $E_i$  and  $E_m$ , are respectively:

$$\Phi_i = 1/(4\pi\epsilon_0) [ \sum_k q_k / R_{ik} + \sum_j Z_j / R_{ij} ]; \quad E_i = q_i \Phi_i \quad (1)$$

$$\Phi_m = 1/(4\pi\epsilon_0) [ \sum_k q_k / R_{km} + \sum_j Z_j / R_{jm} ] \quad E_m = Z_m \Phi_m \quad (2)$$

$$E_{\text{Coul,AB}} = \sum_i E_i + \sum_m E_m \quad (3)$$

When e-pixels of two approaching molecules overlap, besides the un-physical aspect of the matter, numerical singularities in the  $R^{-1}$  dependence may result for very short pixel-pixel distances; all pixel-pixel distances shorter than half the stepsize of the pixel mesh are reset at half the stepsize (the 'collision avoidance' procedure).

## Polarization energies

Let  $\varepsilon_i$  be the total electric field exerted by surrounding molecules at pixel  $i$ ,  $\alpha_i$  the polarizability at pixel  $i$ , and  $\mu_i$  the dipole induced at pixel  $i$  by that field. The linear polarization energy is:

$$E_{\text{Pol},i} = -1/2 \mu_i \varepsilon_i = -1/2 \alpha_i \varepsilon_i^2 \quad (4)$$

$\alpha_i$  is approximated in the PIXEL scheme as  $\alpha_i = (q_i/Z_{\text{atom}}) \alpha_{\text{atom}}$ , where  $Z_{\text{atom}}$  and  $\alpha_{\text{atom}}$  are the atomic charge and polarizability of the atom to whose basin the pixel belongs (from standard repertories). The sum of  $\alpha_i$  's is equal to the total volume polarizability of the molecule.

As before, when e-pixels of two molecules overlap pixel-pixel distances are subjected to the 'collision avoidance' scheme (see above); then, the polarization energy at pixel  $i$  is damped as:

$$E_{\text{Pol},i} = -1/2 \alpha_i [\varepsilon_i d_i]^2 \quad \text{for } \varepsilon < \varepsilon_{\text{max}}, \quad d_i = \exp(-\varepsilon_i / (\varepsilon_{\text{max}} - \varepsilon_i)) \quad (5)$$

and  $E_{\text{Pol},i} = 0$  for  $\varepsilon > \varepsilon_{\text{max}}$ . The limiting field,  $\varepsilon_{\text{max}}$  is an adjustable empirical parameter in the formulation. The total polarization energy at a molecule is the sum of polarization energies at each of its electron density pixels,  $E_{\text{Pol,TOT}} = \sum E_{\text{Pol},i}$ .

## Dispersion energies

Dispersion energies are calculated as a sum of pixel-pixel terms in a London-type expression:

$$E_{\text{Disp,AB}} = (-3/4) \sum_{i,A} \sum_{j,B} E_{\text{OS}} f(R) \alpha_i \alpha_j / [(4\pi\varepsilon^0)^2 (R_{ij})^6] \quad (6)$$

$$f(R) = \exp[-(D/R_{ij} - 1)^2] \quad (\text{for } R_{ij} < D) \quad (7)$$

where  $\alpha_i$  are the distributed polarizabilities of eq.(4), and  $D$  is an adjustable empirical parameter.  $E_{\text{OS}}$  (the 'oscillator strength') can be evaluated by considering each pixel as a separate oscillator, with a formal ionization potential  $I_i$ , which in turn is a function of the ionization potential,  $I^\circ$ , of the atom to whose basin the pixel belongs, and of the distance  $R_i$  between the pixel and the atomic nucleus. This last formulation, eq. (8b), is entirely empirical as are the parameters  $\beta$  (see Table). The equations are:

$$E_{\text{OS}} = (I_i I_j)^{1/2} \quad (8a)$$

$$I_i = I^\circ \exp(-\beta R_i) \quad (8b)$$

## Repulsion energies

The total charge density overlap integral between molecules A and B is calculated over the original uncontracted charge densities. Therefore, the repulsion energy does not depend on the contraction (condensation) level. The integration is done numerically by counting all pairs of overlapping charge density elements, for each of which the integral is  $\rho(i)*\rho(j)*dV$ ,  $dV$  being the charge density elementary volume. The procedure is sensitive to the stepsize and to the accuracy of symmetry transformations. Pairs of symmetry related molecules in crystals (e.g. translation  $+x$  and translation  $-x$ ) may have slightly different overlap integrals. In this case the best guess is the average of the two, so that total energies are not affected. Maximum differences are 0.1-0.2 kJ/mol for first-row elements, and 0.5-1.0 kJ/mol for overlaps involving higher halogens.

Since each charge density element is assigned to an atomic basin, the total overlap is subdivided into contributions from pairs of atomic species  $m$  and  $n$ ,  $S_{mn}$ . The expressions are:

$$S_{AB} = \sum_{i,A} \sum_{j,B} [\rho_i(A) \rho_j(B)] V \quad (9)$$

$$E_{Rep,mn} = (K_1 - K_2 \Delta\chi_{mn}) S_{mn} \quad (10a)$$

$$E_{rep,tot} = \sum_{m,n} E_{rep,mn} \quad (10b)$$

where  $\Delta\chi_{mn}$  is the corresponding difference in Pauling electronegativity, and  $K_1$  and  $K_2$  are positive disposable parameters. For atoms with  $Z > 30$  (in this case Br and I) the presence of the  $d$ -electrons in the valence shell produces larger overlap and hence a slight (8%) decrease in  $K_1$  is introduced. The total repulsion energy is the sum over all  $m-n$  pairs.

The total intermolecular Pixel interaction energy is:

$$E_{Tot} = E_{Coul} + E_{Pol} + E_{Disp} + E_{Rep} \quad (11)$$

The empirical parameters in the Pixel formulation were optimized considering 1) the agreement between calculated lattice energies and experimental heats of sublimation for organic crystals, 2) interaction energies between molecular dimers in comparison with ab initio calculations, and 3) semi-quantitative agreement between Pixel partitioned energies and Intermolecular Perturbation Theory (IMPT) partitioned energies. The numbers are  $\epsilon_{max} = 150 \cdot 10^{10} \text{ V m}^{-1}$  in eq. (5),  $D = 3.0 \text{ \AA}$  in eq. (7),  $K_1 = 4800$  and  $K_2 = 1200$  in eq. (10) for energies in  $\text{kJ mol}^{-1}$  with electron densities in  $\text{electrons \AA}^{-3}$ . While these are suggested as universal parameters, very minor adjustments can be made to fit any desired thermochemical or structural property of the particular system under investigation, without substantial loss of physical realism.

**Table** Physical properties of atoms in the Pixel formulation

atom	atomic radius, Å	atomic polarizability, Å <sup>3</sup>	electro- negativity	ionization potential, au	
				I°	β
H	1.10	0.39	2.1	0.500	0.4
C aliphatic	1.77	1.05	2.5	0.414	0.8
C aromatic	1.77	1.35	2.5	0.414	0.9
C aromatic bridge	1.77	1.90	2.5	0.414	1.05
N	1.64	0.95	3.0	0.534	0.5
O	1.58	0.75	3.5	0.500	0.4
F	1.46	0.50	4.0	0.640	0.0
Cl	1.76	2.30	3.0	0.477	0.35
S	1.81	3.00	2.5	0.381	0.4
Br	1.87	3.27	2.80	0.434	0.1
I	2.03	5.50	2.50	0.384	0.1

See also A.Gavezzotti, *Molecular Aggregation*, Oxford University Press, Oxford 2007, pp.304ff.; for the latest additions and changes see the PIXEL code, file all.dat.for.