Potentials

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I. INTRODUCTION

This is a short description of potential forms used by the ORIENT program. The description presented here is a summary of the more detailed and complete explanation in 'The Theory of Intermolecular Forces' by A. J. Stone [1].

II. THE POTENTIAL FUNCTIONAL FORM

The site-site potentials we use are of the form

$$U = \sum_{a} \sum_{b} U^{ab},\tag{1}$$

where *a* and *b* label sites in molecules A and B, and U^{ab} is therefore the interaction potential between this pair of sites. In the following discussion we will look at only the repulsion and dispersion terms in U^{ab} . The electrostatic and polarization terms will be considered later.

The form of U^{ab} that we will use is

$$U^{ab} = K e^{\alpha_{ab}(r_{ab} - \rho_{ab}(\Omega_{ab}))} - \frac{C_6^{ab}}{r_{ab}^6}.$$
 (2)

Here K is a convenient energy unit (taken to be 10^{-3} Hartree), r_{ab} is the distance between the sites, ρ_{ab} is the shape-function for the pair of sites and C_6^{ab} is the dispersion coefficient for this pair of sites.

Higher-order dispersion terms can be added without a problem. But, for now, let us ignore any angular part to the dispersion contribution. All the angular dependence — the anisotropy — is in the short-range repulsion term. This term is very likely the dominant source of anisotropy, but there is good reason to believe that the dispersion term is also quite anisotropic in systems with large anisotropies such as the benzene dimer[2]. Further, we have ignored any anisotropy in the hardness parameter α_{ab} . This is a deliberate simplification and I am not aware of any systematic tests to see if it is a good one.

The shape function $\rho_{ab}(\Omega_{ab})$ is best described in local axis systems that reflect the local symmetries of the sites *a* and *b*. These symmetries could be approximate. For example, a convenient choice for the local *z*-axis at a carbon atom in a benzene molecule might be to have it point from the carbon to the bonded hydrogen atom. With this choice of *z*-axis, an approximate cylindrical symmetry may be imposed. In which case, the potential parameters would be quite simple. But we now need to transform from these local axis systems to the global axis as the molecular configurations are defined in the global, or laboratory frame. This transformation is done using the *S*-functions defined by eqs. 3.3.7 in ref. [1] and is given by (eq. 11.3.6 in ref. [1])

$$\rho_{ab}(\Omega_{ab}) = \sum_{l_a l_b j k_a k_b} \rho_{l_a l_b j}^{k_a k_b} \bar{S}_{l_a l_b j}^{k_a k_b}.$$
(3)

I am not going to go into details about these S-functions as I do not fully understand them. But here is the information needed to define the potentials we will be using.

We do not use the most general S-function in our potentials, but only the special cases: \bar{S}_{l0l}^{k0} and \bar{S}_{0ll}^{0k} . Since we do not use mixed terms in the sum, this leads to a very intuitive result that the shape function of a pair of sites is the sum of the shape functions of the individual sites. This is so because these special S-functions can be written quite simply as

$$\bar{S}_{l0l}^{k0} = C_{l,k}(\theta, \phi)^*, \tag{4}$$

where the renormalized spherical harmonics (in the Racah definition) are defined as

$$C_{l,k}(\theta,\phi) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\theta,\phi).$$
(5)

We can use the real components of the renormalized spherical harmonics (defined below) to get

$$\bar{S}_{l0l}^{\kappa 0} = C_{l,\kappa}(\theta_a, \phi_a),\tag{6}$$

where the Greek letter κ has been used in place of k to indicate this is the real component and the angles now have subscripts a to indicate they are the polar coordinates describing the site–site vector from a to b in the local axis system of site a. Likewise, we define

$$\bar{S}_{0ll}^{0\kappa} = C_{l,\kappa}(\theta_b, \phi_b). \tag{7}$$

Now we can write the (approximate) shape function as

$$\rho_{ab}(\Omega_{ab}) = \rho^a(\theta_a, \phi_a) + \rho^b(\theta_b, \phi_b), \tag{8}$$

where

$$\rho^{a}(\theta_{a},\phi_{a}) = \sum_{l\kappa} \rho^{a}_{l\kappa} C_{l,\kappa}(\theta_{a},\phi_{a}), \tag{9}$$

with a similar expression for $\rho^b(\theta_b, \phi_b)$.

We can interpret ρ^a as the shape function of site *a*. This is a very useful concept when developing atom–atom potentials with the aim of *transferability*, where it is important to define the parameters in the potential in terms of the properties of the atomic sites.

A. $C_{l,\kappa}(\theta,\phi)$

The real component of the renormalized spherical harmonics is can be defined using the procedure given in Appendix B of Stone's book. By choosing linear combinations of the complex functions, we can define the real and imaginary components as

$$C_{l,mc} = \sqrt{\frac{1}{2} \left((-1)^m C_{l,m} + C_{l,-m} \right)} \\ iC_{l,ms} = \sqrt{\frac{1}{2} \left((-1)^m C_{l,m} - C_{l,-m} \right)} \end{cases} m > 0.$$
(10)

Using $\kappa = 0, 1c, 1s, ..., lc, ls$ we can define $C_{l,\kappa}$ through the above real and imaginary components.

The real components of the renormalized spherical harmonics are related to the regular spherical harmonics by

$$R_{l,\kappa}(\mathbf{r}) = r^{\iota} C_{l,\kappa}(\theta,\phi),\tag{11}$$

which are listed (in terms of the Cartesian components) in Appendix E of Stone's book. Here are the first few in angular form

$$C_{00} = 1$$

$$C_{10} = \cos \theta$$

$$C_{11c} = \sin \theta * \cos \theta$$

$$C_{11s} = \sin \theta * \sin \phi$$

$$C_{20} = \frac{1}{2}(3\cos^2 \theta - 1)$$

$$C_{21c} = \sqrt{3}\sin \theta \cos \theta \cos \phi$$

$$C_{21s} = \sqrt{3}\sin \theta \cos \theta \sin \phi$$

$$C_{22c} = \frac{\sqrt{3}}{2}\sin^2 \theta \cos^2 \phi$$

$$C_{22s} = \frac{\sqrt{3}}{2}\sin^2 \theta \sin^2 \phi$$

B. Units

By default, the ORIENT program uses atomic units for all parameters. For example,

- $K = 10^{-3}$ Hartree
- $[C_6^{ab}]$: Hartree Bohr⁶
- $[\rho_{ab}]$: Bohr

III. POTENTIAL FORMAT

The potential for the pair of sites C1 and C2 is defined in the format

C1	C2			rho	alpha	C6
	00	00	0	6.439025	1.877932	92.969289
	00	10	1	0.181678		
	10	00	1	0.181678		
	00	20	2	0.00000		
	20	00	2	0.00000		
ENI)					

The first line begins with the site labels and the column headers. The subsequent lines are in the form

$$l_a \kappa_a \ l_b \kappa_b \ j \qquad \text{value} \cdots$$
 (12)

- A. J. Stone, *The Theory of Intermolecular Forces* (Clarendon Press, Oxford, 1996).
 A. J. Misquitta and A. J. Stone, Mol. Phys. **106**, 1631 (2008).