APPENDICES

Appendix A

Basis Functions

The basis orbitals used in the linear combination of atomic orbitals to molecular orbital (LCAO-MO) approximation as the basis set in practical calculations are mostly atom-centered functions that resemble orbitals as they can be found for isolated atoms. Many different kinds of basis set functions could be used but only two types of basis functions have been commonly used. Basis orbitals of the first type are called Slater-type orbitals (STO). The radial part of such orbitals is an exponentially decaying function,

$$\chi_v^{STO}(r) = A_v e^{-\xi r} \qquad \text{(i)}$$

For practical calculations these functions have the disadvantage that evaluation of integrals involving such functions is time-consuming. Another type of orbitals is called Gaussian-type orbital in which at a large distance the orbitals decay as a function of $e^{-\alpha r^2}$.

$$\chi_v^{GTO}(r) = B_v e^{-\alpha r^2} \qquad \text{(ii)}$$

The Slater type orbitals more correctly describe the qualitative features of the molecular orbitals in real systems. However all the integrals are relatively easy to evaluate with Gaussian basis functions. Therefore, these orbitals are approximated by a linear combination of Gaussian basis functions (GTO);

$$\chi_v^{STO}(r) \approx \chi_v^{CGF} = \sum_{p=1}^{L} d_{pv} \chi_v^{GTO} \qquad \text{(iii)}$$

The functional form of such a GTO, called contracted Gaussian Function (CGF), is different, especially in the vicinity of the nucleus. Therefore a number of GTO's with different exponents coefficients are necessary to give a reasonable basis orbital. The exponents and contraction coefficients can be determined in different ways, e.g. by fitting to an STO or by optimizing the energy in ab initio calculations on

atoms and small molecules. Once these values are determined they define a standard basis set, and are not changed in further calculations on other molecules.

Standard basis sets: Several standard basis sets are nowadays commonly used nowadays. The so-called minimal basis sets have one basis orbital per two inner shell electrons and one basis orbital for each valence atomic orbital. Thus, for first-row elements there are basis functions resembling 1s, 2s, $2p_x$, $2p_y$, $2p_z$ atomic orbitals. The STO's are replaced by n GTO's (STO-nG). The common minimal basis set is the STO-3G basis.

In the 3-21G basis the 1s AO of a first-row element is represented by a fixed combination of 3 GTO's, the 2s ($2p_x$ etc.) are approximated by a fixed combination of 2 GTO's and the extra valence orbitals 2s'($2p_x$' etc.) are just one GTO. The larger basis sets is 6-31G (1s : 6 GTO's; 2s ($2p_x$ etc.): 3 GTO's; 2s'($2p_x$' etc.): 1 GTO). The usual next step is to go to basis sets which have polarization functions, e.g. d-orbitals for first row elements which allow for a lower symmetry of the electron distribution in a molecule compared to that of an atom.

Appendix B

Universal Force Field (UFF)

Universal force field has been developed as a new force field using general rules for estimating force field parameters based on simple relations. This set of fundamental parameters is based only on the element, its hybridization, and connectivity. The parameters used to generate the Universal force field include a set of hybridization dependent atomic bond radii, a set of hybridization angles, van der Waals parameters, torsional and inversion barriers, and a set of effective nuclear charges. The elements in the Universal force field periodic table are the atom types: atoms of the same type may only be similar chemically and physically, yet, as is the norm, they are treated identically in the force field.

The potential energy of an arbitrary geometry for a molecule is written as a superposition of various two-body, three-body, and four-body interactions. The potential energy is expressed as a sum of valence or bonded interactions and non-bonded interactions:

$$E = E_R + E_\theta + E_\Phi + E_\omega + E_{vdw} + E_{el} \qquad \text{(iv)}$$

The valence interactions consist of bond stretching (E_R). B Angular distorsions are bond angle bonding (E_θ), dihedral angle torsion (E_ϕ), and inversion term (E_ω). The non bonded interactions consist of van der Waals (E_{vdw}) terms and electrostatic (E_{el}) terms.

Appendix C

Basis Set Superposition Error (BSSE)

The Counterpoise Correction

In theory, the excess binding energy, ΔE, due to the interaction of species A and B will be given by Equation iv.

$$\Delta E = E_{AB}^* - \left(E_A + E_B \right) \qquad \text{(v)}$$

Here, E_{AB}^* is the energy of the complex AB and $E_{A,B}$ is the energy of the monomer A, B in its relaxed geometry and its own basis functions. In the limit of an infinite basis set, Equation 4 is true. However, using finite basis sets, the functions on A will improve on those of B, and vice versa, during the optimization of the complex in an artificial manner. This is referred to as *Basis Set Superposition Error* (BSSE), the standard estimate of which may be made by the counterpoise correction of Boys and Bernardi, given by Equation v.

$$\delta_{BSSE} = E_A^* + E_B^* - E_A^\dagger - E_B^\dagger \qquad \text{(vi)}$$

Here, $E_{A,B}^*$ is the energy of monomer A, B in the basis set of AB and the geometry of the complex. $E_{A,B}^\dagger$ is the energy of monomer A, B in its own basis at the geometry of AB. Thus, the actual, corrected, energetic contribution to the formation of the adduct is given by Equation vi.

$$\Delta E_{TOT} = \Delta E - \delta_{BSSE}$$
$$= E_{AB}^* - \left(E_A^* + E_B^* \right) - \left(E_A - E_A^\dagger \right) - \left(E_B - E_B^\dagger \right) \qquad \text{(vi)}$$

For van der Waals complexes, the distortion of the relaxed monomer geometries due to the formation of the complex is usually insignificant, such that $E_{A,B} \approx E_{A,B}^\dagger$. In practice, we have found the actual value of the two right-hand terms for van der Waals clusters to be at most around 10% of the binding energy.