APPENDIX

Appendix A

Basis Sets

A basis set is essentially a finite number of atomic-like functions over which the molecular orbital is formed via Linear combination of Atomic Orbital (LCAO) methods, as summarized in equation i.

$$\psi_a = \sum_{i=1}^{n} c_{ai}\phi \tag{i}$$

Equation a) shows that in a set of n basis functions, all may contribute to the final molecular orbital. There are two main types of orbital used.

Slater-Type Orbitals (STO)

These have the mathematical formulation given in equation ii.

$$\phi_{\zeta,n,\ell,m}(r,\theta,\varphi) = NY_{\ell,m}(\theta,\varphi)r^{n-1}e^{-\zeta r} \tag{ii}$$

N is a normalization constant, Y is a spherical harmonic and ζ is a parameter which defines the spatial extent of the orbital. STO's are not generally used, due to problems with n-body integral generation in larger systems, being replaced by Gaussian-Type Orbitals.

Gaussian-Type Orbitals (GTO)

Gaussian-Type Orbitals take the (polar) form given in equation iii.

$$\phi_{\zeta,n,\ell,m}(r,\theta,\varphi) = NY_{\ell,m}(\theta,\varphi)r^{2n-2-\ell}e^{-\zeta r^2} \tag{iii}$$

Gaussian orbitals generally do not represent the cusp of the wavefunction (at r = 0) as well as STO's, but nevertheless are used as any n-body integrals required for STO calculations may be represented by a 2-body integral using GTO's. To better model the cusp, a series of primitive (individual) gaussian functions, referred to as a contracted gaussian function, are used; each primitive has a pre-optimized coefficient, the sum over which takes a similar form to an STO. Each contracted gaussian has a only a single optimizable orbital expansion coefficient for reasons of computational efficiency.

Split (Valence) Basis Sets

Whereas in a minimal basis set there is only one function of each type (e.g, 1s, 2s, $2p_x$, a split basis set will use two functions (e.g., 1s, 1s', 2s, 2s', $2p_x$, $2p_x$'). The importance of this inclusion is in a situation where the ζ-component is unlikely to give a reasonable representation of the same orbital when orientating along a different axis.

A good example of this is in a system where s-p_z σ-bonding and p_x-p_y π-bonding occur in a single molecule. Obviously, the σ-orbital will be more localized than the π-orbital, and thus the p_z and $p_{x,y}$ ζ-components will not adequately describe the spatial extent of each other. The split basis sets allow for this possibility by having two separately optimizable gaussian functions for p_z and $p_{x,y}$, i.e., that the radial distribution of a given orbital type is no longer assumed to be isotropic about the centre of expansion.

It should be noted that this is mostly an issue for the bonding and geometry of a system, so that the core orbitals are often left as single functions for reasons of computational efficiency (a split valence basis set). The example above, with two independent functions of one type is called a double-zeta basis; a set of three independent functions is referred to as a triple-zeta basis, four as a quadruple-zeta, etc. The most popular types of basis functions used, i.e., the Pople and Dunning series, are of at least double-zeta basis type.

Appendix B

Hay-Wadt VDZ (n+1) ECP Basis Set

The Hay-Wadt (n+1) effective core potentials include an extra shell of electrons beyond what is traditionally available in effective core potentials. For example, on potassium the 3s and 3p electrons are not subsumed into the core as they would be in other ECP's. This set is derived from the exponents and contraction coefficients given in the Hay-Wadt paper and were obtained directly from P. J. Hay. The elements beyond Kr include the 1-electron Darwin and mass-velocity relativistic corrections in their definitions.

Elements Contraction
K – Ca : (5s,5p) → [3s,3p]
Sc – Cu : (5s,5p,5d) → [3s,3p,2d]
Rb – Sr : (5s,6p) → [3s,3p]
Y – Ag : (5s,6p,5d) → [3s,3p,2d]
Cs – Ba : (5s,6p) → [3s,3p]
La – Au : (5s,6p,5d) → [3s,3p,2d]

Basis set and ECP for Silver atom

```
AG  0
 S   3  1.00
   2.95000000          -1.79105640
   2.14900000           2.02445700
   0.66840000           0.60728390
 S   4  1.00
   2.95000000           1.01411250
   2.14900000          -1.24139710
   0.66840000          -0.49014270
   0.99700000E-01       1.11283750
 S   1  1.00
   0.34700000E-01       1.00000000
 P   3  1.00
   6.55300000          -0.10791170
   1.56500000           0.74036450
   0.57480000           0.37210080
 P   2  1.00
   0.90850000          -0.41837100E-01
   0.83300000E-01       1.00875860
 P   1  1.00
   0.25200000E-01       1.00000000
```

```
 D   3  1.00
   3.39100000              0.13969380
   1.59900000              0.47444210
   0.62820000              0.51563110
 D   1  1.00
   0.21080000              1.00000000
 ****
```

Effective Core Potentials

```
AG  0
AG-ECP   3   28
f potential
 5
0    568.70062370        -0.05879300
1    162.35790660       -20.11451460
2     51.10257550     -104.27331140
2     16.92058220      -40.45397870
2      6.16695960       -3.44200090
s-f potential
 5
0    76.09746580         2.98615270
1    15.33273590        35.15764600
2    18.77153450       450.18099060
2    13.36632940      -866.02483080
2     9.82369480       523.11101760
p-f potential
 5
0    56.33180430         4.96406710
1    69.06090980        21.50282190
2    19.27179980       546.02754530
2    12.57706540      -600.38225560
2     8.79566700       348.29492890
d-f potential
 5
0    53.46410780         3.04674860
1    40.19754570        23.36567050
2    11.90860730       777.25401170
2     9.75281830     -1238.86024230
2     8.17889970       608.06771210
```

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.

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

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.

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

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.

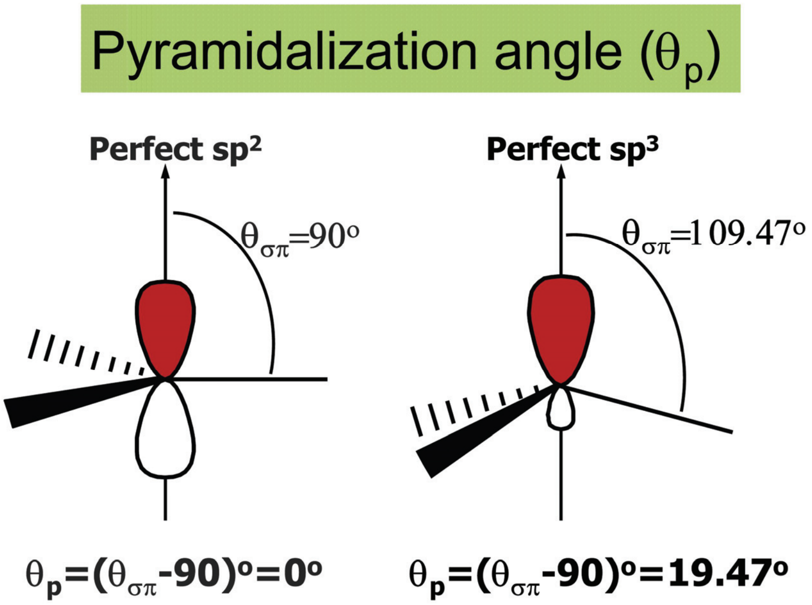
$$\begin{aligned} \Delta E_{TOT} &= \Delta E - \delta_{BSSE} \\ &= E_{AB}^{*} - \left(E_A^{*} + E_B^{*}\right) - \left(E_A - E_A^{\dagger}\right) - \left(E_B - E_B^{\dagger}\right) \qquad \text{(vi)} \end{aligned}$$

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.

Appendix D

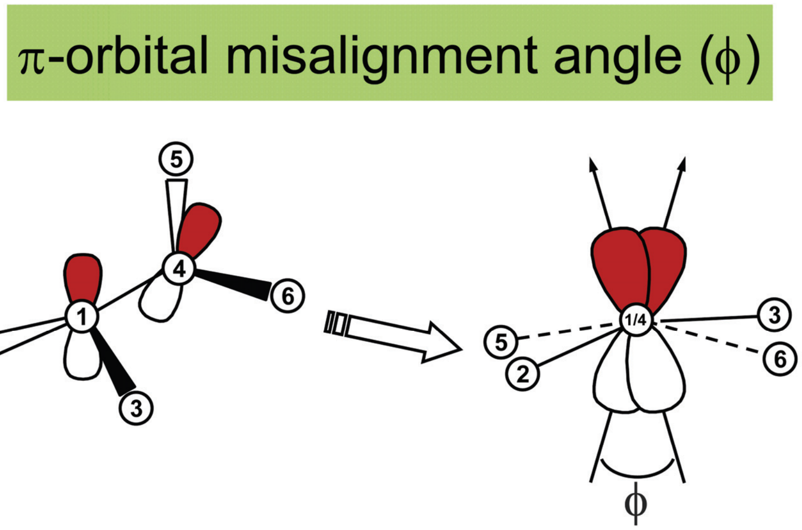
The π-orbital axis vector analysis (POAV)

Pyramidalization angle (θ_p)



The reactivity of the nanocluster materials is primarily driven by the enormous strain engendered by their uncommon geometry as reflected in the pyramidalization angles of the carbon atoms. As shown in the illustration above, for an sp^2-hybridized (trigonal) carbon atom, planarity is strongly preferred, and this implies a pyramidalization angle of θ_p=0°, whereas an sp^3-hybridized (tetrahedral) carbon atom requires θ_p=19.47°. All of the carbon atoms in C60 have θ_p=11.6°, and it is immediately clear that their geometry is more appropriate for tetrahedral than trigonal hybridization. Thus, the chemical conversion of any trivalent carbon atom in C_{60} to a tetravalent carbon atom relieves the strain at the point of attachment and mitigates the strain at the 59 remaining carbon atoms. Hence, reactions that serve to saturate the carbon atoms are accelerated by strain relief, and this strongly favors fullerene addition chemistry. Just as in the case of a fullerene, a perfect SWNT is without functional groups; therefore these quasi-1D cylindrical aromatic macromolecules are chemically inert. However, curvature-induced pyramidalization of the carbon atoms induces a local strain, and carbon nanotubes are expected to be more reactive than a flat graphene sheet.

π-orbital misalignment angle (ϕ)



Beside the pyramidalization angle, the strain in nonplanar conjugated organic molecules also arises from the π-orbital misalignment angle (ϕ shown above) between adjacent pairs of conjugated carbon atoms. There are very few π-orbital misalignment angles in the fullerenes, and in the case of C60 the π-orbital alignment is perfect ($\phi=0^{o}$). This index allows comparisons in reactivity between the carbon atoms in a given fullerene such as C70 or SWNT.

Although all carbon atoms in SWNT are equivalent, there are two types of bonds: those that run parallel to the armchair line and those on atoms in the zigzag line with π-orbital misalignment angles 0° and ~10°, respectively. On the basis of calculations of torsional strain energies in conjugated organic molecules, π-orbital misalignment is likely to be the main source of strain in the carbon nanotubes. Just as in the case of the fullerenes, the reactivity of carbon nanotubes arises out of their topology but for different reasons. Furthermore, since the pyramidalization angles and the π-orbital misalignment angles of SWNTs scale inversely with the diameter of the tubes, a differentiation is expected between the reactivity of carbon nanotubes of different diameters.

Appendix E

Natural Bond Orbital (NBO)

The Orbital Interaction Analysis

In order to analyze the interactions of the metal cations with the corresponding ligand, Natural Bond Orbital analysis was performed on the optimized polyatomic wave function. Natural Bond Orbital analysis transforms the input basis set $\{\chi_i\}$ to various localized natural atomic orbitals NAOs, , bond orbitals NBOs, et cetera.

The localized sets may be subsequently transformed to delocalized natural orbitals (NOs) or canonical molecular orbitals (MOs). Each step of the above sequence involves an orthonormal set that spans the full space of the input basis set and can be used to give an exact representation of the calculated wave function and the expectation values of selected operators (properties) of the system.

The localized sets may be subsequently transformed to delocalized natural orbitals (NOs) or canonical molecular orbitals (MOs). Each step of the above sequence involves an orthonormal set that spans the full space of the input basis set and can be used to give an exact representation of the calculated wave function and the expectation values of selected operators (properties) of the system.

The NAO orbitals allow the calculation of an improved Natural Population Analysis correcting some of the Mulliken population analysis deficiencies. Once the NAOs are evaluated, the core orbitals (with occupancies >1.999 e) are set. Following, among the one-center blocks, the lone-pairs (with occupancies > 1.90 e) are defined, and finally, the bond-vectors (occupancy > 1.90 e) are located among the two center blocks. In this way a "natural Lewis structure" is obtained.

For a comprehensible clarification in the nature of the complexation, NBO analysis was carried out. The key descriptor in this analysis is what is known as the second order perturbative stabilization energy for “donor-acceptor” (bond-antibond) natural orbital interaction. The stabilization energies arise from those interactions in the complexes, which lead to the loss of electron occupancy from the localized NBOs to the empty ones. They are also referred to as "delocalization" corrections. For the donor NBO(i) and the acceptor NBO(j), the stabilization energy $\Delta E^{(2)}_{(i,j)}$ associated with delocalization i → j is evaluated by

$$\Delta E^{(2)}_{(i,j)} = 2\frac{(F_{(i,j)})^2}{\varepsilon_j - \varepsilon_i} \qquad \text{(vii)}$$

Where and are diagonal elements (orbital energies), and $F_{(i,j)}$ is the off-diagonal NBO Fock matrix element. The electron density transfer (EDT) corresponding to such natural orbital i → j interaction can be estimated by

$$\rho_{i \to j} \simeq 2\frac{(F_{(i,j)})^2}{(\varepsilon_j - \varepsilon_i)^2} \simeq \frac{\Delta E^{(2)}_{(i,j)}}{(\varepsilon_j - \varepsilon_i)} \qquad \text{(viii)}$$

Either the stabilization energy or the electron density transfer would reveal the strength of such donor-acceptor orbital interaction.