Supplementary Material (ESI) for PCCP

Supporting information for 'Formulations of the closed-shell interactions in endohedral systems'

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1 Derivations for the quasi-spherical and nanotube irregular polarizabilities, eqns (97-98)

We start the derivation of eqns (97-98) from a London-like formula for the dipole-dipole dispersion interaction between two C_{2v} monomers using the expression [1]

$$\Delta E^{(2)}_{\mathrm{disp,DD}} \approx -\frac{1}{4}\frac{I_A I_B}{I_A + I_B}\frac{\alpha^A_{XX}\alpha^B_{XX} + \alpha^A_{YY}\alpha^B_{YY} + 4\alpha^A_{ZZ}\alpha^B_{ZZ}}{R^6}. \tag{1}$$

Here I_A and I_B are the ionization potentials of monomers A and B respectively. The α_{XX}, α_{YY} and α_{ZZ} are the principal-axis components of the polarizability tensors of the monomers, assumed to be parallel with the intermolecular coordinate system (XYZ). Note that the contribution from the intermolecular axis Z is four times larger than the two contributions perpendicular to Z. The R is the intermolecular distance.
Consider first a spherical shell with a polarizability density $\rho_{ii} = d\alpha_{ii}/ds$, ds being a surface element on the surface S. From eqn (1), assuming $\alpha^A_{XX} = \alpha^A_{YY} \equiv \alpha^A_\perp$ and $\alpha^A_{ZZ} \equiv \alpha^A_\parallel$, we obtain

$$\Delta E = -\frac{1}{4}\frac{I_A I_B}{I_A + I_B}\int_S \left[2\alpha^A_\perp \rho^B_\perp + 4\alpha^A_\parallel \rho^B_\parallel\right] R^{-6} ds. \tag{2}$$

For an isotropic case, $\alpha^A_\perp = \alpha^A_\parallel = \alpha^A$, $\rho^B_\perp = \rho^B_\parallel = \rho^B$, giving

$$\Delta E = -6\pi\frac{I_A I_B}{I_A + I_B}\alpha^A \rho^B R^{-4}. \tag{3}$$

A comparison with eqn (69) of the main paper gives for a sphere

$$\bar{\alpha}^{\dagger B}_1 = 8\pi\rho^B R^{-4}. \tag{4}$$

For an isotropic A on the axis, z, of a nanotube B we similarly get

$$\Delta E = -\frac{1}{4}\frac{I_A I_B}{I_A + I_B} 6\alpha^A \rho^B (2\pi R) \int_{-\infty}^{\infty} \frac{dz}{r^6} = -6\pi R \alpha^A \rho^B \frac{I_A I_B}{I_A + I_B} \int_0^{\infty} \frac{dz}{(R^2 + z^2)^3}, \tag{5}$$

where R is the radius of the tube, and r the distance from A to the surface element. Using eqn (3.249.1) of Ryzhik and Gradshteyn [2],

$$\Delta E = -\frac{9}{8}\pi^2 \rho \alpha^A \frac{I_A I_B}{I_A + I_B} R^{-4}, \tag{6}$$

yielding for the thin-walled cylinder

$$\bar{\alpha}_1^{\dagger B} = \frac{3}{2}\pi^2 \rho^B R^{-4}. \tag{7}$$

The sphere/tube ratio for the same R becomes $16/3\pi$. We repeat that this line of thought would only be valid if the contributions to eqn(1) could be independently integrated, which for the fullerenes is a bad approximation.

2 Explicit figures for the He_2, He_3, and $A\cdots C_6H_6$ model systems

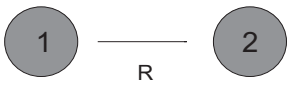

Figure 1: The geometry of the He_2 system.

Figure 2: The geometry of the He_3 system.

Additional references

[1] J. Muñiz, C. Wang, and P. Pyykkö, unpublished manuscript.
[2] I. S. Gradshteyn and I. M. Ryzhik, Tables of Integrals, Sums, Series and Products (in Russian), Fizmatgiz, Moscow, 1963, p. 308.

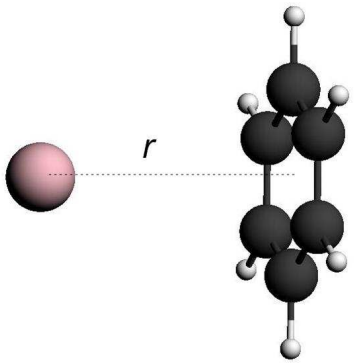

Figure 3: The geometry for the $A \cdots C_6H_6$ model system. r was taken as 4.0 $\mathring{A}$.