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 \cite{1}

$$\Delta E^{(2)}_{\text{disp,DD}} \approx -\frac{1}{4} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A^{XX} \alpha_B^{XX} + \alpha_A^{YY} \alpha_B^{YY} + 4 \alpha_A^{ZZ} \alpha_B^{ZZ}}{R^6}. \quad (1)$$

Here $I_A$ and $I_B$ are the ionization potentials of monomers $A$ and $B$ respectively. The $\alpha_{XX}$, $\alpha_{YY}$ and $\alpha_{ZZ}$ are the principal-axis components of the polarizability tensors of the monomers, assumed to be parallel with the intermolecular coordinate system ($X Y Z$). 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 $\rho_i = d\alpha_{ii}/ds$, $ds$ 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

$$\Delta E = -\frac{1}{4} \frac{I_A I_B}{I_A + I_B} \int_S \left[ 2 \alpha_A^{\perp} \rho_B^{\perp} + 4 \alpha_A^{\parallel} \rho_B^{\parallel} \right] R^{-6} ds. \quad (2)$$

For an isotropic case, $\alpha_A^{\perp} = \alpha_A^{\parallel} = \alpha_A^A$, $\rho_A^{\perp} = \rho_A^{\parallel} = \rho_B^B$, giving

$$\Delta E = -6 \pi \frac{I_A I_B}{I_A + I_B} \alpha_A^A \rho_B^B R^{-4}. \quad (3)$$

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

$$\bar{\alpha}_1^B = 8 \pi \rho_B^B R^{-4}. \quad (4)$$
For an isotropic A on the axis, z, of a nanotube B we similarly get

\[ \Delta E = -\frac{1}{4} \frac{I_A I_B}{I_A + I_B} 6 \alpha^A \rho^B (2\pi R) \int_{-\infty}^{\infty} \frac{dz}{r^6} = -6 \pi R \alpha^A \rho^B \frac{I_A I_B}{I_A + I_B} \int_{0}^{\infty} \frac{dz}{(R^2 + z^2)^3}, \]  

(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],

\[ \Delta E = -\frac{9}{8} \pi^2 \rho^A \frac{I_A I_B}{I_A + I_B} R^{-4}, \]  

(6)

yielding for the thin-walled cylinder

\[ \bar{\alpha}^B = \frac{3}{2} \pi^2 \rho^B R^{-4}. \]  

(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 \( \text{He}_2 \), \( \text{He}_3 \), and \( A \cdots C_6H_6 \) model systems

![Figure 1: The geometry of the \( \text{He}_2 \) system.](image1)

Figure 1: The geometry of the \( \text{He}_2 \) system.

![Figure 2: The geometry of the \( \text{He}_3 \) system.](image2)

Figure 2: The geometry of the \( \text{He}_3 \) system.

Additional references
Figure 3: The geometry for the \( A \cdots C_6H_6 \) model system. \( r \) was taken as 4.0 Å.