Notes and Equations for Many Body Theory and Counterpoise Corrections

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1 Basic Many Body Expansion (MBE)

The many body expansion is a simple expansion of a many-body system's properties (like energy) into a sum of contributions from individual bodies (monomers) and the interactions between them (n-body terms). If all interactions are considered for an N-body system (terms n = 1, ... , N are included) then the method is exact.[1] Any k-body interaction term is simply the contribution of the k-mer minus all lower-body interactions and the monomer contributions. Approximations are made by only considering up to k-body terms, where $k < N$. A property like total energy ($E_{IJK...N}$) can then be written as the sum of the monomer contributions (E_i) with all desired n-body interaction terms($\epsilon^{(n)}$):

$$E_{IJK...N} = \sum_{i=1}^{N} E_i + \sum_{i=1}^{N}\sum_{j>i}^{N} \epsilon_{ij}^{(2)} + \sum_{i=1}^{N}\sum_{j>i}^{N}\sum_{k>j}^{N} \epsilon_{ijk}^{(3)} + ... \tag{1a}$$

$$\epsilon_{ij}^{(2)} = E_{ij} - E_i - E_j \tag{1b}$$

$$\begin{aligned}
\epsilon_{ijk}^{(3)} &= E_{ijk} - (\epsilon_{ij}^{(2)} + \epsilon_{ik}^{(2)} + \epsilon_{jk}^{(2)}) - (E_i + E_j + E_k) \\
&= E_{ijk} - (E_{ij} - E_{ik} - E_{jk}) + (E_i + E_j + E_k)
\end{aligned} \tag{1c}$$

2 Counterpoise Correction Schemes

In order to account for the Basis Set Superposition Error (BSSE, as described in other documents) various "counterpoise correction" schemes have been implemented. A few of them are described here.

2.1 Boys-Bernardi Counterpoise (CP)[2]

The CP scheme is solely a method of correcting for the BSSE inherent in the calculation of interaction energies of dimers. That being said, it is used as a starting point for all other relevant counterpoise corrections used today. For a dimer AB, the interaction energy ($\epsilon_{AB}^{(2)}$) can be calculated as the difference between the energy of the dimer (E_{AB}) and the energies of the monomers (E_A and E_B). To combat BSSE, the CP scheme simply calculates all values in the dimer basis:

$$\epsilon_{AB}^{(2)} = E_{AB}(AB) - E_A(AB) - E_B(AB) \tag{2}$$

where the basis set used is in parenthesis.

2.2 Site-Site Function Counterpoise (SSFC)[3]

The SSFC scheme is a direct generalization of the CP scheme applied to MBE's of any order. All interaction terms are calculated in the "full cluster basis," or the basis of the N-mer such that equation (1a) becomes:

$$E_{IJK...N} = \sum_{i=1}^{N} E_i(IJK...N) + \sum_{i=1}^{N}\sum_{j>i}^{N} \epsilon_{ij}^{(2)}(IJK...N) + \sum_{i=1}^{N}\sum_{j>i}^{N}\sum_{k>j}^{N} \epsilon_{ijk}^{(3)}(IJK...N) + ... \tag{3}$$

where equations (1b) and (1c) similarly include the N-mer basis.

References

[1] I. G. Kaplan, *Theory of Molecular Interactions*, Elsevier, Amsterdam, 1986.

[2] S. Boys and F. Bernardi, *Molecular Physics*, 1970, **19**, 553–566.

[3] B. H. Wells and S. Wilson, *Chem. Phys. Lett.*, 1983, **101**, 429–434.