

Notes and Equations for Many Body Theory and Counterpoise Corrections

August 16, 2017

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 $n = 1, \dots, N$ 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 ($E_{IJK\dots N}$) can then be written as the sum of the monomer contributions (E_i) with all desired n -body interaction terms ($\epsilon^{(n)}$):

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

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

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

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:

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

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:

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

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

2.3 Valiron-Mayer Function Counterpoise (VMFC)⁴

A different generalization of the CP scheme is the VMFC scheme. Instead of using the full cluster basis for everything, each k -body contribution term is calculated in the k -

mer basis- the original monomer energies are calculated in the monomer basis, dimer corrections in the dimer basis, etc. It should be noted that even the monomers calculated for the dimer correction are calculated in the dimer basis as well, resulting in the following:

$$E_{IJK...N} = \sum_{i=1}^N E_i(I) + \sum_{i=1}^N \sum_{j>i}^N \epsilon_{ij}^{(2)}(IJ) + \sum_{i=1}^N \sum_{j>i}^N \sum_{k>j}^N \epsilon_{ijk}^{(3)}(IJK) + ... \quad (4a)$$

$$\epsilon_{ij}^{(2)}(IJ) = E_{ij}(IJ) - E_i(IJ) - E_j(IJ) \quad (4b)$$

$$\begin{aligned} \epsilon_{ijk}^{(3)}(IJK) &= E_{ijk}(IJK) - (\epsilon_{ij}^{(2)}(IJK) + \epsilon_{ik}^{(2)}(IJK) + \epsilon_{jk}^{(2)}(IJK)) \\ &\quad - (E_i(IJK) + E_j(IJK) + E_k(IJK)) \\ &= E_{ijk}(IJK) - (E_{ij}(IJK) - E_i(IJK) - E_j(IJK)) \\ &\quad + (E_i(IJK) + E_j(IJK) + E_k(IJK)) \end{aligned} \quad (4c)$$

One can see that even if all interactions are considered, the VMFC total energy will not add up to the full cluster energy. This is possibly a correction to "intramolecular" BSSE effects. It also removes from each subcluster contribution an "unphysical" dependence on the basis functions of other unrelated subclusters.

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.
- [4] P. Valiron and I. Mayer, *Chemical Physics Letters*, 1997, **275**, 46–55.