On the Boys–Bernardi Method to correct Interaction Energies calculated using Møller–Plesset Perturbation Theory

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The Boys and Bernardi method has been used to correct the interaction energy of a molecular association involving two molecules of alanine interacting through their respective carboxylic groups; while the SCF calculation predicts the association to be very stable as expected considering the two hydrogen bonds involved, the second-order Møller–Plesset perturbation theory provides a strongly repulsive interaction energy; it is shown that a number of virtual orbitals with a relatively large contribution from a ghost basis set may be responsible for this.

We recently[1,2] carried out a systematic study on the basis set superposition error in the calculation of the interaction energies of systems of biological interest. The calculations were performed at the SCF level. We are now extending this by the inclusion of correlation, starting with second-order Møller–Plesset perturbation theory (MP2)[3] and some of the preliminary results indicate that unexpected problems arise, of which there are no previous reports, when the counterpoise (CP) method of Boys and Bernardi[4] is applied to correct the basis set superposition error (BSSE) at this level of the theory.

MP2 calculations have been carried out to estimate the interaction energy of two alanine molecules interacting through their respective carboxylic groups giving rise to a double hydrogen-bonded association, the distance between the carboxylic oxygen in one of the molecules and the hydroxylic hydrogen in the other one being 3.3 a.u. (atomic units) (Figure 1 and appendix in ref. 2). The standard 6-31G** basis set was used (26 atoms, 96 electrons, and 250 contracted functions were involved in our dimer calculations). Both chemical intuition and the SCF calculations predict such a conformation to be very stable.[2] However, MP2 prediction is completely different. In fact, the MP2 monomer energy is −322.80347 a.u. and the MP2 dimer energy is −645.63834 a.u., which yields an (uncorrected) interaction energy of −19.7 kcal mol^{-1} as expected. However, once one takes into account the CP method to correct for the BSSE, the interaction energy becomes +14.4 kcal mol^{-1} (MP2 monomer + ghost energy is −322.83067 a.u.).

The analysis of the virtual molecular orbitals (involved in the MP2 summation) in the monomer + ghost calculations shows that some of them which are rather close to the LUMO (and therefore are able to make relatively large contributions to the MP2 energy) present a much larger contribution from the ghost's basis set than from the monomer's basis set. Moreover, their eigenvalues do not correlate with any of the eigenvalues arising from the monomer or dimer calculations. All of this seems to indicate that such virtual molecular orbitals must be considered as a mathematical artefact generated by the use of ghost basis sets and accordingly they should not be taken into consideration in the MP2 calculation. It has been found that the magnitude of these non-physical contributions to the MP2 interaction energy can account for the discrepancies between SCF and MP2 interaction energies.

On the other hand, regarding the origin of the 'ghost molecular orbitals,' the Hartree–Fock equations in the molecular basis (no ghost orbitals) are as in equation (1) (using an orthogonal AO basis for simplicity).

$$h^F U = U\varepsilon \quad (1)$$

The introduction of a set of ghost orbitals extends the basis, and the Hartree–Fock matrix may be partitioned as in (2), where '1' is the molecular basis and '2' the ghost orbitals. If the ghost orbitals are remote from the molecular basis then equations (3) and (4) hold, where T, V, and $(J - K)$ are the kinetic energy, nuclear attraction, and electron repulsion matrices. However, since the only source of potential is the molecule, remote from the ghost orbitals, equations (5) and (6) lead to equation (7), which has the same solution as equation (1) plus a set of (positive) eigenvalues and associated eigenvectors. These new 'ghost molecular orbitals' are not occupied and so take no part in the SCF energy expression.

$$\begin{pmatrix} h_{11}{}^{F} & h_{12}{}^{F} \\ h_{21}{}^{F} & h_{22}{}^{F} \end{pmatrix} \tag{2}$$

$$h_{12}{}^{F} = h_{21}{}^{F+} \simeq 0 \tag{3}$$

$$h_{22}{}^{F} = T_{22} + V_{22} + (J - K)_{22} \tag{4}$$

$$V_{22} + (J - K)_{22} \simeq 0 \tag{5}$$

$$h_{22}{}^{F} = T_{22} \tag{6}$$

$$h^{F}U = \begin{pmatrix} h_{11}{}^{F} & 0 \\ 0 & T_{22} \end{pmatrix} \begin{pmatrix} U_{11} & 0 \\ 0 & U_{22} \end{pmatrix} = \begin{pmatrix} U_{11} & 0 \\ 0 & U_{22} \end{pmatrix} \varepsilon \tag{7}$$

The kinetic energy of an STO is $1/2\zeta^2 > 0$ and so, if the ghost basis contains diffuse functions, the new eigenvalues may be close to zero (and positive); a new set of low-lying molecular orbitals very suitable for CI or MP2 but with no physical meaning will be available.

We believe that excitations into these low-lying non-physical 'ghost molecular orbitals' are the source of the surprising MP2 interaction energy result.

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