

An Examination of Basis Set Superposition Error at the Correlated Level: Illuminating the Role of the Exchange Repulsion

Clinton S. Nash*

*Department of Chemistry and Physics, University of New England,
11 Hills Beach Road, Biddeford, Maine 04005*

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Abstract: A reformulated ‘virtuals-only’ counterpoise procedure for the correction of basis set superposition error is introduced and applied to an examination of the interaction energy of the helium dimer. This method allows a direct calculation of the exchange (Pauli) repulsion at the correlated level. Our findings suggest that at the correlated level the Pauli repulsion may be interpreted as a decrease in the monomer correlation energy calculated using the dimer virtual space relative to that with a monomer-only virtual space. This observation provides further theoretical justification for the Full Counterpoise procedure in preference to any virtuals-only counterpoise procedure.

Introduction

The use of various methods to remove basis set superposition error (BSSE) from ab initio quantum chemical calculations has become standard practice. The recognition that the application of such a correction is crucial to a quantitative description of bonding, particularly those in weakly interacting systems, has focused attention on those methods. The most important of these are the *a priori* Chemical Hamiltonian Approach (CHA) and symmetry-adapted perturbation theory (SAPT) and the *a posteriori* Function Counterpoise Correction (FCP) of Boys and Bernardi.^{1–3} Because of its conceptual simplicity and ease of implementation, the latter is much more commonly applied than either of the former and is the focus of this contribution. That BSSE is an unphysical computational artifact brought about by the artificial extension of the variational space available to a monomer, A, in an interacting system AB is in fact demonstrated by application of the FCP procedure. Namely, the energy of the monomer A calculated at some level of theory in the combined basis set of the dimer, AB, is lowered relative to its energy found using only its own basis set. In the function counterpoise procedure this energy difference is simply subtracted from the energy of the dimer (along with difference between the energy of B calculated in the

dimer basis and in only its own) evidently leaving a total energy devoid of basis set superposition error.

Almost from its original introduction, however, objections were raised that the Bernardi and Boys full counterpoise correction overestimates the BSSE.^{4–6} The rationale for these objections, particularly for correlated calculations, is based on the Pauli exclusion principle and a perceived imbalance in the treatment of a dimer on one hand and the individual monomers on the other. In a correlated counterpoise calculation on a monomer (i.e. using the basis set of the dimer), excitations to (amplitudes of) orbitals corresponding to occupied MOs of B are allowed, whereas in the dimer they are not. Accordingly, contributions from these ‘spurious’ excitations would lead to an FCP monomer energy that is too low, an overall counterpoise correction that is too large, and therefore a potential energy surface that is too shallow. Although various ad hoc procedures with varying degrees of theoretical justification have been advanced to compensate for that anticipated overcorrection, most are unsatisfactory.⁷

To address the issue directly Daudey et al. devised a ‘virtuals-only’ counterpoise procedure (VCP) in which only the virtual SCF orbitals of the ‘ghost’ atom B are used to augment the molecular orbital basis set of monomer A in a correlated CP calculation on A.⁴ In principle, this should lead to a smaller monomer counterpoise correction than the full counterpoise procedure and ultimately a less shallow interaction potential energy surface. In subsequent years, several

* Corresponding author e-mail: cnash@une.edu.

studies have been conducted comparing efficacy of the full and virtuals-only counterpoise procedures.^{8–11} Though the issue remains somewhat contentious, most of the recent work seems to endorse the use of the FCP method, especially when larger, more complete basis sets are used.^{12,13} At the same time, some authors, notably Gutowski et al., have advanced formal arguments supporting the correctness of the FCP and have argued that excluding the ‘to be occupied’ orbitals from the FCP virtual space leads to an underestimation of the exchange repulsion in the AB supermolecule.^{10,14}

We have reexamined this issue in the case of the helium dimer and focused on the role of the Pauli repulsion using a new virtuals-only counterpoise procedure that is similar in philosophy to but substantially different from that proposed by Daudey. As the weakest possible interaction, this choice for a molecular system provides a sensitive test of the various counterpoise correction prescriptions and allows comparisons with an extensive body of existing literature. Our new approach raises new questions about the counterpoise procedure and suggests that a new interpretation of the role that the ‘spurious’ orbitals play may be in order. In particular, we have found it appropriate to reinterpret the exchange (Pauli) repulsion at the correlated level as a disruption of the correlation energy of each monomer in a supermolecular aggregate by the presence of occupied orbitals located on its partner(s).

Theoretical Methods

For all of the *ab initio* calculations done in our examination of BSSE in the helium dimer we have used Dunning’s aug_cc-pVXZ ($X=T, Q, 5$) basis sets and a slightly modified version of the GAMESS quantum chemistry package.^{16–18} Our variant of the virtuals-only counterpoise procedure (vVCP), to be described below, was conducted using a custom program designed for that purpose. The various counterpoise corrections were carried out according to the standard formulas (eq 1 below). The energy of the interacting dimer AB (here, $A=B=He$) determined at some level of theory (SCF, MP2, CCSD, etc.) is modified by the difference between the energy of each of the monomers A and B calculated in the union of their basis sets $(A \cup B)_{XCP}$ and their energies calculated using their individual basis sets.

$$E_{AB}^{XCP} = E_{AB} - (E_A^{XCP} + E_B^{XCP}); X = F, vV, V$$

$$E_A^{XCP} = E_A(A \cup B)_{XCP} - E_A(A)$$

$$E_B^{XCP} = E_B(A \cup B)_{XCP} - E_B(B) \quad (1)$$

We have calculated MP2, CCSD, and CCSD(T) interaction energies for the helium dimer at a series of 11 internuclear distances between 4.5 and 14 Bohr using each of the correlation-consistent basis sets. These surfaces were corrected using the full counterpoise procedure (FCP) as well as our variant of the virtuals-only counterpoise procedure (vVCP). For comparison, Daudey’s virtuals-only counterpoise procedure (VCP) was also applied to the He_2 PES calculated under aug_cc-pVTZ atomic orbital basis set. The various molecular orbital basis sets symbolized by $(A \cup B)_{XCP}$

have been constructed according to the requirements of each counterpoise correction scheme, X ($X=F, vV, V$).

In Daudey’s original formulation of the virtuals-only counterpoise procedure (VCP), the basis set of a monomer, A, is augmented by only the virtual SCF orbitals of the ghost monomer B.⁴ These ghost virtuals are projected onto the orthogonal subspace of the molecular orbital basis set of A and reorthogonalized to it using Löwdin’s symmetric orthogonalization procedure.¹⁹ The result is an orthonormal molecular orbital basis set useful in correlated VCP calculations which omits orbitals occupied in the AB dimer.

In contrast, our variant VCP formulation (vVCP) is more closely related to the standard counterpoise procedure and in fact reduces to it at the SCF level. Rather than projecting the virtual ghost orbitals of B onto the orthogonal subspace of the monomer A, we perform a typical full counterpoise SCF calculation (i.e. SCF on monomer A using the $A \cup B$ atomic orbital basis set) and project out of the resulting virtual space functions corresponding to the n_B ($=1$ for helium) occupied orbitals of the ghost atom B. These have been generated using a separate fragment (atomic) SCF calculation under the same atomic basis set used for B in both the FCP and AB supermolecule. Prior to the application of the projection operator, these occupied ‘ghost’ functions are orthogonalized to the occupied orbitals of A. The linear dependency that results in the supermolecular MO basis is resolved by deleting the $n_{B,occ}$ functions identified as being most similar to the original occupied ghost orbital(s) of B. The remaining molecular orbital basis set of dimension $N_A + N_B - n_{B,occ}$ (where N_A and N_B are the numbers of atomic basis functions for fragment A and B, respectively) is then renormalized and orthogonalized using Löwdin’s procedure in order to minimize the differences between the original FCP MO basis set and our vVCP MO basis set. The result of this procedure is a virtual space having the orbital structure of a hypothetical noninteracting AB dimer.

In our view, this vVCP method has several features that distinguish it from Daudey’s approach. First, the ghost orbitals of B to be removed from CP virtual space are constrained to be orthogonal to the occupied orbitals of A as they must in the supermolecule. Second, it is a simple matter to return the excised functions to the virtual space and thereby produce a MO basis that spans the same space as the original FCP MO basis. In addition, there is no ambiguity about what constitutes the ‘missing’ orbital—it is identically the SCF function corresponding to the occupied ghost orbital(s) in the supermolecule. Finally, the vVCP virtual space is more similar to the FCP virtual space than that produced using the standard VCP method.

Results

As indicated in Table 1 and Figures 1A, 2A, and 3A, both our uncorrected and FCP-corrected results for the helium dimer are consistent with those of numerous previous studies. The current state-of-the-art theoretical and available experimental results indicate a He_2 interaction energy of ~ 11 K at an internuclear distance of $5.6 a_0$, values we approach using the more extensive basis sets.^{20–31} Indeed, for the aug_cc-pVXZ ($X=T, Q, 5$) basis sets used here, the uncorrected as

Table 1. He₂ Interaction Energies (in K) Calculated Using aug_cc-pVXZ (X=D,T,Q,5) Basis Sets with No BSSE Correction Scheme, the Full and Virtuals-Only Counterpoise Correction (FCP, VCP), and the Variant Virtuals-Only Counterpoise Correction (vVCP) Described Herein^a

basis set	MP2	CCSD	CCSD(T)
DZ			
no CP	11.45 K @ 5.74 a ₀	12.56 K @ 5.69 a ₀	13.37 K @ 5.69 a ₀
FCP	4.01 K @ 6.18 a ₀	5.30 K @ 6.07 a ₀	5.86 K @ 6.01 a ₀
vVCP	n/a	7.68 K @ 5.69 a ₀	8.51 @ 5.65 a ₀
TZ			
no CP	6.99 K @ 5.84 a ₀	8.82 K @ 5.74 a ₀	9.92 K @ 5.72 a ₀
FCP	5.62 K @ 5.89 a ₀	7.42 K @ 5.79 a ₀	8.45 K @ 5.74 a ₀
VCP		8.17 K @ 5.68 a ₀	9.48 K @ 5.62 a ₀
vVCP	n/a	11.60 K @ 5.42 a ₀	13.19 K @ 5.37 a ₀
QZ			
no CP	6.85 K @ 5.84 a ₀	8.78 K @ 5.72 a ₀	10.03 K @ 5.67 a ₀
FCP	6.25 K @ 5.84 a ₀	8.20 K @ 5.72 a ₀	9.44 K @ 5.67 a ₀
vVCP	n/a	13.11 K @ 5.37 a ₀	14.99 K @ 5.32 a ₀
5Z			
no CP	6.89 K @ 5.79 a ₀	8.88 K @ 5.72 a ₀	10.20 K @ 5.67 a ₀
FCP	6.62 K @ 5.79 a ₀	8.68 K @ 5.72 a ₀	10.00 K @ 5.67 a ₀
vVCP	n/a	13.84 K @ 5.32 a ₀	15.97 K @ 5.27 a ₀

^a The data reported correspond to the minima for each basis set and computational method among the He–He distances sampled. Note: by construction, the vVCP scf energy is identical to the FCP scf energy.

well as the FCP-corrected (and VCP-corrected) well depths agree reasonably well with these available data despite the fact that even the aug_cc-pV5Z basis set is evidently not sufficient to fully capture the exquisitely weak interaction in the helium dimer. Numerous excellent studies of the helium dimer potential energy surface have been published which employ basis sets of aug_cc-pV6Z quality or better several of which include midbond functions. Though results of such studies and especially recent quantum Monte Carlo calculations^{24,26,27} more closely approximate the basis set limit and the experimental result than do ours, our focus is to examine the role of the virtual orbitals and their relationship to BSSE and the Pauli repulsion, and therefore these differences are immaterial.^{20–31}

As expected, use of the FCP procedure to correct BSSE leads to shallower potential energy surfaces compared to uncorrected calculations, though the room for improvement and therefore the degree of that improvement is much smaller for the larger basis sets. And, as expected, the He₂ PES corrected using Daudey's VCP method is deeper than the corresponding FCP surface and shallower than the uncorrected one. This indicates that notwithstanding questions of its usefulness, the smaller VCP orbital space does attenuate the counterpoise correction. What is striking is the remarkable difference that the vVCP results give with respect to those of other counterpoise methods. Not only are the vVCP potential energy surfaces in each case deeper by as much as half (e.g., 15.9 K vs 11 K) than the current best estimates but also the minima occur at much shorter internuclear distances (~5.4 a₀ vs 5.6 a₀).²⁰

Figures 1B, 2B, and 3B illustrate the variation of helium CCSD(=CISD) FCP and vVCP counterpoise corrections to the correlation energy relative to the pure atomic result as a function of internuclear separation (strictly, monomer-ghost separation) for, respectively, the augmented TZ, QZ, and 5Z basis sets. This analysis reveals the source of the unantici-

pated vVCP well deepening. As expected and in keeping with the variational principle, the FCP correction calculated for each basis set is negative at all monomer-ghost distances indicating some degree of improvement in the description of the monomer electronic structure by the presence of virtual orbitals located on the ghost. Also according to expectations, the magnitude of the FCP correction at each internuclear separation decreases with increasing quality of atomic basis set, and at the same time the calculated correlation energy asymptotically approaches the pure atomic result as the value of R increases. All of this explains why the FCP corrected potential energy surfaces for all basis sets are to varying degrees shallower than the uncorrected ones. However, particularly for the aug_cc-pV5Z basis, the correction is minimal, and the uncorrected and FCP-corrected potential energy surfaces are nearly coincident.

In contrast, at many atom-ghost distances the vVCP monomer correlation energies are actually *higher* (less negative) than their corresponding pure atomic results, a finding that is actually exacerbated for larger basis sets which are presumably closer to completeness. While at first this may seem a violation of the variation principle (which applies here because of the equivalence of CCSD and CISD for two-electron systems) it is not. Unlike Daudey's VCP procedure, the vVCP virtual space is not simply an augmentation of the set of monomer by virtual ghost orbitals but rather consists of the standard FCP virtual space with one function, identical to the ghost He 1s orbital of the noninteracting partner, projected out of it. So, the structure of the vVCP virtual space more closely resembles that of the dimer in that orthogonality of the 'core' 1s electrons on each monomer (or, if you will monomer and ghost) is preserved. Therefore, from the perspective of an atomic calculation, though the (AUB)_{vVCP} supermolecular orbital basis set may be 'larger' than the pure AO basis set, it is not necessarily 'better' than the monomer basis in its capacity to minimize calculated

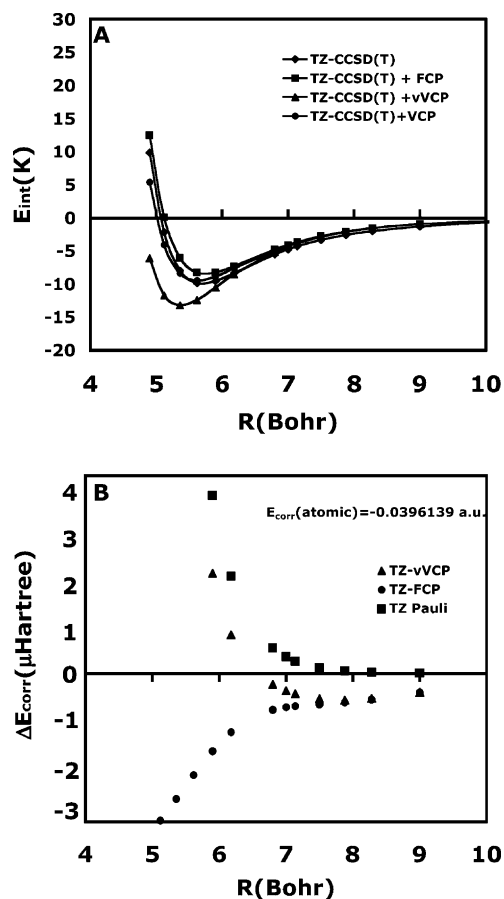


Figure 1. (A) CCSD(T) potential energy surfaces for the Helium dimer calculated with the aug_cc-pVTZ basis sets using no BSSE correction; and the full (FCP), virtuals-only (VCP), and variant virtuals-only (vVCP) counterpoise procedures. (B) FCP and vVCP counterpoise corrections relative to the atomic He CCSD(=CISD) correlation energy calculated using the aug_cc-pVTZ basis set. $\Delta E_{\text{corr}} = E_{\text{XCP}} - E_{\text{atom}}$.

total atomic energies. In any case, this ‘negative’ counterpoise correction calculated with the vVCP procedure at short distances tends to deepen and contract the calculated potential energy surfaces.

Some additional points merit mention here. First, we note that as the monomer-ghost distance increases the vVCP correction energy does change sign and once again becomes positive, though less so than for the FCP correction because of the smaller virtual space. This is best illustrated in Figure 1B though it is qualitatively similar in Figures 2B and 3B (the CP correction here is small compared to the scale of the graph). And as it should, the asymptotic behavior of the vVCP correction resembles and becomes identical to the FCP results as the monomer-ghost distance increases. Finally, in all cases we have found that if the ‘excised’ orbital(s) in the vVCP case is simply reappended to the virtual space the corresponding FCP result is fully recovered.

It is clear that the anomalous counterpoise correction calculated at the CCSD(=CISD) level using the vVCP method cannot be reasonably construed as the result of a basis set superposition error. Instead, the data suggest that the degradation of monomer electron correlation in a dimer, independent of any electrostatic or bonding interaction, may

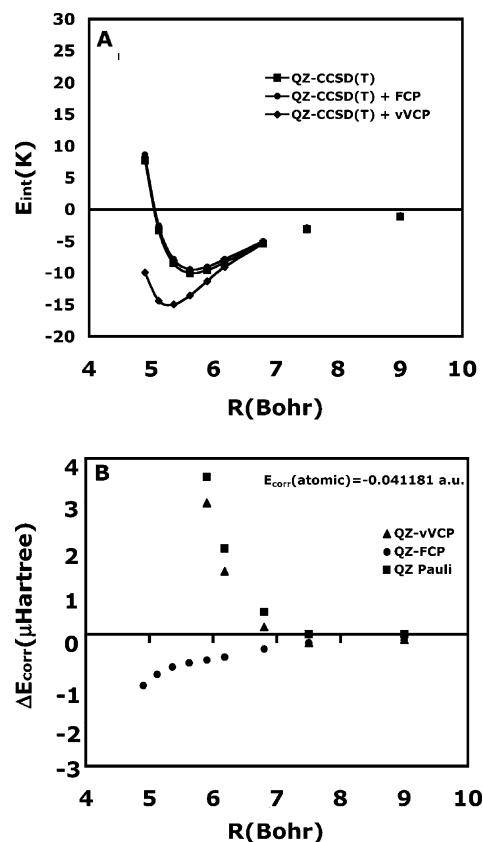


Figure 2. (A) CCSD(T) potential energy surfaces for the Helium dimer calculated with the aug_cc-pVQZ basis sets using no BSSE correction; and the full (FCP), and variant virtuals-only (vVCP) counterpoise procedures. (B) FCP and vVCP counterpoise corrections relative to the atomic He CCSD(=CISD) correlation energy calculated using the aug_cc-pVQZ basis set. $\Delta E_{\text{corr}} = E_{\text{XCP}} - E_{\text{atom}}$.

be interpreted as an effective repulsion which we conclude corresponds to the exchange (Pauli) repulsion calculated at the correlated level (the correlation exchange repulsion, CER). This interpretation follows from the fact that the disruption of monomer correlation is the result of the mere presence of ‘occupied’ (i.e. excluded) orbitals on the ghost partner. It is clear that this repulsive energy component is also present in a true dimer calculation, and, therefore, the removal of this important repulsive energy component according to the vVCP method produces the anomalously deep and compact potential energy well. Any basis set superposition error would tend to mitigate the effect of removing this correlation exchange repulsion, which explains why our seemingly anomalous vVCP results become more pronounced with more complete basis sets. This monomer correlation exchange repulsion is also depicted in Figures 1B, 2B, and 3B for each basis set. The curves labeled XZ Pauli (X=T,Q,5) are generated by correcting the corresponding vVCP curve for BSSE by subtracting the FCP counterpoise correction.

Figure 4 depicts a comparison of the He_2 SCF exchange repulsion calculated with the calculated monomer correlation exchange repulsion (the latter corrected for BSSE). The total exchange repulsion is taken as the sum of the SCF exchange repulsion and two times the monomer correlation exchange repulsion. Importantly, the correlation exchange repulsion

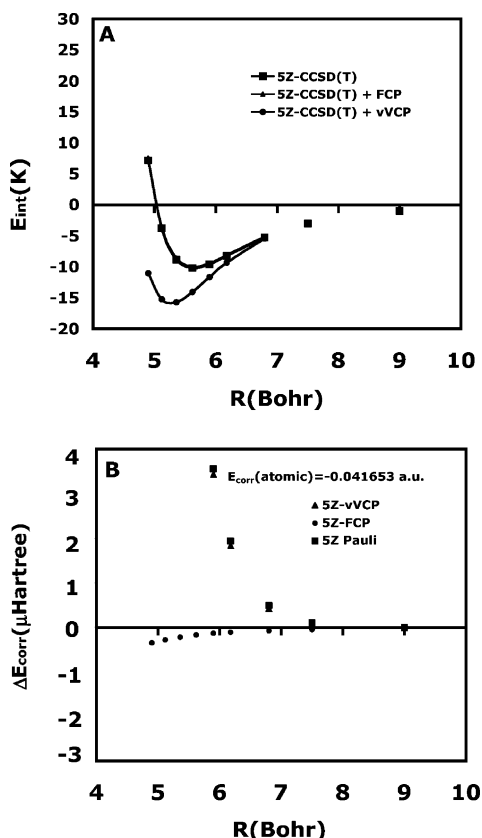


Figure 3. (A) CCSD(T) potential energy surfaces for the helium dimer calculated with the aug_cc-pV5Z basis sets using no BSSE correction; and the full (FCP), and variant virtuals-only (vVCP) counterpoise procedures. (B) FCP and vVCP counterpoise corrections relative to the atomic He CCSD(=CISD) correlation energy calculated using the aug_cc-pV5Z basis set. $\Delta E_{\text{corr}} = E_{\text{XCP}} - E_{\text{atom}}$.

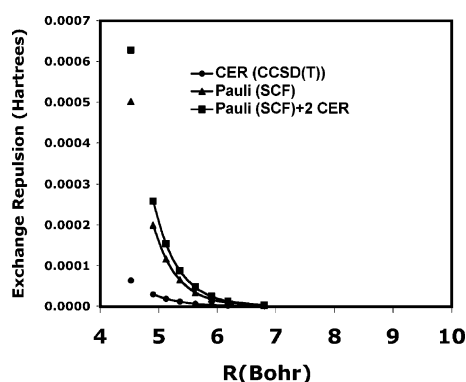


Figure 4. The helium dimer exchange repulsion at the SCF level, Pauli (SCF), and the effective monomer correlation exchange repulsion (CER) calculated at the CCSD(=CISD) level. Also depicted is the total exchange repulsion. The data correspond to values calculated using the aug_cc-pVQZ basis set.

exhibits qualitatively the same dependence on monomer-ghost distance as the SCF exchange repulsion. Finally, the fact that our observation of this phenomenon, which is not per se a basis set superposition error, does not decrease but rather increases with larger basis sets suggests that basis set incompleteness is not the issue here.

Conclusions

The formal arguments advanced by Gutowski et al., to support the use of the full counterpoise procedure hold among other things that it, in contrast to virtuals-only approaches, permits a proper description of the electron density in the internuclear (intermonomer) region. Because of this, use of any virtuals-only counterpoise method necessarily degrades a description of exchange repulsion.^{10–14} While our results corroborate this finding, we should emphasize that our interpretation of the reason for this underestimation is somewhat different. From our perspective, exchange repulsion at the correlated level is manifested as a disruption of the correlation energy of the monomer calculated in the dimer (supermolecule) molecular orbital basis set relative to that calculated in only the monomer's own basis set. By performing a correlated monomer calculation according to the vVCP prescription and subtracting the result from the supermolecular PES, we actually remove this essential component of the interaction energy. Daudey's VCP method, or any other technique that merely supplements the monomer virtual space with additional functions, approximates this effect and therefore does lead to an understatement of the exchange repulsion. Finally, use of the vVCP method directly illuminates the role that the 'occupied' partner orbitals play and permits a full evaluation of the exchange repulsion at the correlated level.

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