

P. Reinhardt

Dressed second-order Epstein–Nesbet perturbation theory and consequences of orbital delocalization for the BSSE correction in dimer systems (in honor of J.-P. Malrieu)

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Abstract The dressed diagonal approximation to the self-consistent – size consistent CI, corrected for off-diagonal Fock matrix elements in localized orbitals is developed and applied to the ammonia dimer system. A quite correct correlation energy can be obtained for this system, with a significantly reduced dependence of the results on the choice of the localization procedure. When calculating an interaction energy, the choice of the monomer orbitals and the application of the Boys–Bernardi counterpoise procedure shows in this case an unusual behavior: the correlation energy does not increase with the size of the atomic basis sets. Nevertheless a reasonable potential curve can be obtained.

Keywords Perturbation theory · Basis set superposition error · Intermolecular interactions · Diagram expansion · Localized orbitals

1 Introduction

Calculating accurate intermolecular interaction energies for weakly interacting systems remains a challenging task, especially when considering the obtained data as inputs for the construction of simpler multi-center potentials for simulations of realistic chemical and biological systems. For relatively small interacting systems, super-molecular calculations may be performed even at most sophisticated levels of theory like CCSD(T), but for larger systems, these methods may be no longer applicable while less expensive DFT calculations fail to describe dispersion interactions correctly.

Perturbation theory, if it can compete with the precision of the other methods, is still available as an alternative. In practice, second-order Møller–Plesset [1] perturbation theory (MP2) is a widely used and relatively reliable tool for calculating intermolecular interaction energies. However, MP2

misses important contributions to the correlation energies as well for the dimer as for the monomer systems, and a cancellation of these terms is responsible for the generally good performance. In the present article, we would like to present variants of another perturbation series, including infinite-order summations of Møller–Plesset diagrams, namely the commonly known, but nowadays rarely used Epstein–Nesbet perturbation theory, which remained since the 60s in the interest of J.-P. Malrieu’s work [2–8].

The basic form of Epstein–Nesbet perturbation theory [9, 10] is obtained when choosing the unperturbed Hamiltonian being the diagonal of the exact Hamiltonian in a determinantal basis (Hartree–Fock reference determinant Φ_0 and excited determinants Φ_I ; Φ_J be as well the reference Φ_0):

$$\mathbf{H} = E_{\text{HF}}|\Phi_0\rangle\langle\Phi_0| + \underbrace{\sum_I |\Phi_I\rangle\langle\Phi_I|\mathbf{H}|\Phi_I\rangle\langle\Phi_I|}_{\mathbf{H}_0^{\text{EN}}} + \underbrace{\sum_I \sum_{J \neq I} |\Phi_I\rangle\langle\Phi_I|\mathbf{H}|\Phi_J\rangle\langle\Phi_J|}_{\mathbf{V}^{\text{EN}}}. \quad (1)$$

This form of perturbation theory is known to be notoriously difficult to assess due to the interplay of summations and shifts in denominators, which hinder factorizations and separations of partial sums of specific interactions or diagrams. Localizing molecular orbitals may help to circumvent several of the difficulties as was shown in model cases [5]. For the present study, the example of a molecular dimer has been chosen since for this relatively simple system with a straightforward understanding of localization and delocalization we may study the addressed problems in detail – localizing means here primarily separating the molecular orbitals to be centered on one or the other monomer. An extension of the results to be presented towards periodic systems may be a subsequent step. In fact, the development of the combinations of various series of perturbation theory had its origin in the research for a perturbative calculation of the correlation energy for periodic systems, as CI-based methods in

P. Reinhardt
Laboratoire de Chimie Théorique,
Université Paris VI, 4 place Jussieu,
75252 Paris, France
E-mail: Peter.Reinhardt@upmc.fr
Fax: +33-1-44-274117

localized orbitals still seem very demanding for these applications [11].

The article is structured as follows: in a first section we recall Epstein–Nesbet perturbation theory at second order, and we introduce the diagonal dressings as possible variants, including without significant extra cost, substantial contributions from higher excitations beyond the space spanned by doubly excited determinants. Non-zero off-diagonal Fock matrix elements, as to be included due to the orbital localization, will be accounted for in a simple approximation, leading to an overall method which is rather inexpensive to apply.

After a brief presentation of the computational details we come to the numerical results. In that section we will show the performance of the proposed combination of different infinite summations of diagrams for the NH₃ dimer and we will discuss an unexpected behavior of the correction for the Basis Set Superposition Error (BSSE) following the Boys–Bernardi procedure [12] as an essential element of the accurate calculation of any interaction energy. Section 5 presents the conclusion and closes the article.

2 Theoretical considerations

2.1 Dressed Epstein–Nesbet perturbation theory

Epstein–Nesbet perturbation theory can either be developed directly from the partitioning of the Hamiltonian (Eq. 1) or it may be obtained from two other starting points: we may add to the basic second-order diagram in Møller–Plesset perturbation theory the infinite series of all those higher-order diagrams which repeat the (spin-)orbital indices (Fig. 1).

Or we take the matrix formulation of the infinite-order Møller–Plesset perturbation series in all double excitations (DMBPT-∞, or commonly called Coupled Electron Pair Approximation, CEPA-0)

$$\sum_{ijab} \langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle c_{ij}^{ab} = E_{\text{Corr}}$$

$$\langle \Phi_0 | \mathbf{H} | \Phi_{ij}^{ab} \rangle - E_{\text{HF}} + \sum_{klcd} \langle \Phi_{kl}^{cd} | \mathbf{H} | \Phi_{ij}^{ab} \rangle c_{kl}^{cd} = 0 \quad (2)$$

and restrict the matrix to the first line/column and the diagonal (i, j, \dots denote here occupied spinorbitals (or holes), and a, b, \dots stand for virtual spinorbitals (or particles); the coefficients c_{ij}^{ab} determined by the second line in Eq. 2 enter the expression for the correlation energy in the first line). Both approaches may be found in standard textbooks [13].

The theory of intermediate Hamiltonians [14] led to the construction of the Full CEPA or (SC)²CI in adding to the

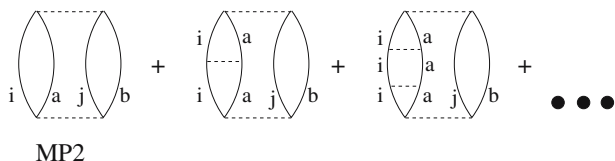


Fig. 1 Part of the infinite series of same-index diagrams

CEPA-0 equations all linked excitations in so-called exclusion-principle-violating diagrams, which repeat one or more indices in quadri- or higher excited determinants [15]. The summation of these diagrams can be cast into a (self consistent) shift of the diagonal of the Hamilton matrix in the determinantal basis, which permits to address a large variety of CI or CEPA-based correlation methods [11], even up to CCSD with estimations of connected triple excitations [16, 17]. The interest in these methods lies in the fact that at the cost of a theory including only doubly-excited determinants, a large number of higher excited determinants are accounted for in the calculation of the correlation energy (but not in the wavefunction).

Since the basic Epstein–Nesbet second-order correlation energy makes use of the diagonal of the CEPA-0 equations, the same dressings may be applied, leading as well to a self-consistent procedure. We may call these dressed Epstein–Nesbet second-order perturbation theory, summing as many higher-order diagrams as possible without significantly increasing the computational effort of the procedure. The diagonal approximation of the (SC)²CI was already derived implicitly as set of 2×2 eigenvalue problems in the articles of Lepetit and Malrieu [18, 19]. From the multitude of possible dressings in this more general view – we dispose of all possible dressings of CEPA-based matrix methods – we will use only two in the present article: the dressing of the averaged coupled pair functional of Gdanitz et al. [20] (ACPF) and the (SC)²CI scheme. For the former, we add to the diagonal of the Hamiltonian an averaged effect of the EPV diagrams through a term $\Delta_{ij}^{ab} = -(2/n)E_{\text{Corr}}$ with n being the number of electrons in the system. In order to obtain the dressing for the (SC)²CI, we perform the summation over all EPV diagrams individually as

$$\Delta_{ij}^{ab} = - \sum_{\text{EPV}(i,j,a,b)} \langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ijkl}^{abcd} \rangle c_{kl}^{cd}$$

$$= - \sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 | \mathbf{H} | \Phi_{kl}^{cd} \rangle c_{kl}^{cd} \quad (3)$$

for each index couple i, j, a, b . EPV(i, j, a, b) means here that at least one of the indices k, l, c, d is equal to one of i, j, a, b . This summation can be partially pre-calculated and presents no significant additional work, as was shown in reference [19]. We may note that the reduction $\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ijkl}^{abcd} \rangle = \langle \Phi_0 | \mathbf{H} | \Phi_{kl}^{cd} \rangle$ holds only for orthogonal orbitals, otherwise cofactors of the overlap matrix have to be introduced. The coefficients c_{ij}^{ab} of the first-order wavefunction are obtained from

$$\langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle + \left(\langle \Phi_{ij}^{ab} | \mathbf{H}' | \Phi_{ij}^{ab} \rangle + \Delta_{ij}^{ab} \right) c_{ij}^{ab} = 0 \quad \text{or}$$

$$c_{ij}^{ab} = - \frac{\langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle}{\langle \Phi_{ij}^{ab} | \mathbf{H}' | \Phi_{ij}^{ab} \rangle + \Delta_{ij}^{ab}}, \quad (4)$$

where we set $\langle \Phi_I | \mathbf{H}' | \Phi_J \rangle = \langle \Phi_I | \mathbf{H} - E_{\text{HF}} \delta_{IJ} | \Phi_J \rangle$. This becomes a system of equations to be solved iteratively, since the wavefunction coefficients c_{kl}^{cd} enter the dressing Δ_{ij}^{ab} , and thus the reduction defines a recursion from doubly excited determinants to any level of excitation. The first line

of Eqs. 4 corresponds to the diagonal approximation of the dressed CEPA-0 (see Eq. 2 with the dressing Δ_{ij}^{ab}), whereas the second line is the formula from first-order perturbation theory with shifted denominators. Finally, the expression for the correlation energy for the dressed Epstein–Nesbet perturbation theory at second order reads

$$E_{\text{Corr}}^{(2)} = \sum_{ijab} \sum_{\text{Spins}} \langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle c_{ij}^{ab} \\ = - \sum_{ijab} \sum_{\text{Spins}} \frac{|\langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle|^2}{\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ij}^{ab} \rangle + \Delta_{ij}^{ab}}. \quad (5)$$

We may note that the spin settings of the orbitals in the sum has to be carried on explicitly, since the dressings may take different forms for different combinations. For Epstein–Nesbet theory without dressing an explicit formula has been given to extract only one single contributing spin combination [21] or to average over all possible settings [22].

2.2 Using localized orbitals

Upto this point, all the discussion of perturbation theory and summation of EPV diagrams assumed implicitly the Møller–Plesset partition of the Hamiltonian in a mono-electronic part and a bi-electronic one. This decomposition is straight-forward in canonical orbitals where the Fock matrix is diagonal. If this is not the case, as for localized orbitals, additional interactions and diagrams have to be taken into account, coupling determinants with different indices exactly by these off-diagonal Fock matrix elements. These are either incorporated in the zeroth-order Hamiltonian, and lead not any more to a simple expression for the zeroth-order energy as the sum of the orbital energies, or a second perturbation series in these elements has to be added to the series in bi-electronic matrix elements.

Cast in formulæ, the decomposition of the Hamiltonian reads in canonical orbitals

$$\mathbf{H}_0^{(\text{MP})} = \sum_{\mu} \epsilon_{\mu} a_{\mu}^{\dagger} a_{\mu} \\ \mathbf{V}^{(\text{MP})} = \mathbf{H} - \mathbf{H}_0^{(\text{MP})} = \sum_{\mu, \nu, \rho, \sigma} (\mu\nu | \rho\sigma) a_{\mu}^{\dagger} a_{\rho}^{\dagger} a_{\nu} a_{\sigma} \\ - \sum_{\mu, \nu} \langle \mu | \sum_{i \in \text{occ.}} 2J_i - K_i | \nu \rangle \quad (6)$$

with the orbital energies ϵ_{μ} and bi-electronic integrals $(\mu\nu | \rho\sigma)$, and in localized orbitals then

$$\mathbf{H}_0^{(\text{MP}, \text{loc})} = \sum_{i'} F_{i'i'} a_{i'}^{\dagger} a_{i'} + \sum_{a'} F_{a'a'} a_{a'}^{\dagger} a_{a'}. \quad (7)$$

The extra-diagonal elements of the Fock operator become a mono-electronic part of \mathbf{V}

$$\mathbf{V}_{\text{loc}}^{(\text{MP})} = \mathbf{V}^{(\text{MP})} + \sum_{i' \neq j'} F_{i'j'} a_{i'}^{\dagger} a_{j'} + \sum_{a' \neq b'} F_{a'b'} a_{a'}^{\dagger} a_{b'}. \quad (8)$$

For second-order Møller–Plesset theory this results in the

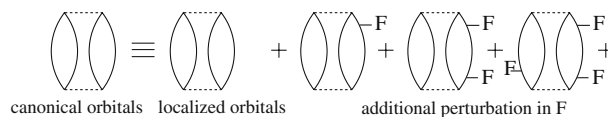


Fig. 2 The series of the infinite summation of off-diagonal Fock matrix elements. Some partial sums in third order, fourth order, and an infinite summation of paired Fock-matrix interactions have been presented in [7]

series of diagrams [23] to be summed over which is depicted in Fig. 2.

The series can be introduced in the CEPA-0 equations by replacing the off-diagonal matrix elements $\langle \Phi_I | \mathbf{H} | \Phi_J \rangle$ by the mono-electronic part $\langle \Phi_I | \mathbf{F} | \Phi_J \rangle$, leading thus to a high-dimensional system of linear equations to be solved. The result will be the MP2 energy as calculated in canonical orbitals and which is commonly implemented in standard program packages working in localized orbitals [24].

A trivial way to evaluate the infinite series of Fig. 2 is to perform a MP2 calculation in canonical orbitals (MP2C), to use the same formula for localized orbitals (MP2L) and to take the difference $\text{MP2C} - \text{MP2L}$. This difference then may be added to the evaluation of the higher-order bielectronic interactions in the (dressed) Epstein–Nesbet series of Eq. (5). Doing so permits to still separate the bi-electronic interaction and the interaction through off-diagonal Fock matrix elements, introduced by the localization procedure. Of course, we should keep in mind that we neglect in this way all combined diagrams of Figs. 1 and 2.

2.3 Consequences of orbital delocalization

After having accounted for the off-diagonal Fock matrix elements we may turn to another impact of using localized orbitals instead of canonical ones: the infinite summation of same-index diagrams which make the difference between MP2 and EN2 perturbation theory, manifests itself in additional Coulomb and exchange matrix elements in the energy denominator, the numerators $|\langle \Phi_0 | \mathbf{V} | \Phi_{ij}^{ab} \rangle|^2$ being the same for both:

$$\underbrace{F_{ii} + F_{jj} - F_{aa} - F_{bb}}_{\text{Møller–Plesset}} \\ \rightarrow \underbrace{F_{ii} + F_{jj} - F_{aa} - F_{bb} - \tilde{J}_{ij} - \tilde{J}_{ab} + \tilde{J}_{ia} + \tilde{J}_{ib} + \tilde{J}_{ja} + \tilde{J}_{jb}}_{\text{Epstein–Nesbet}} \quad (9)$$

for an index quadruple $ijab$ and the generalized, spin-dependent combination of Coulomb and exchange integral $\tilde{J}_{ij} = J_{ij} - K_{ij} \delta_{\sigma_i \sigma_j}$ (Fig. 3).

We may consider just one orbital s on either fragment of the dimer system, and form a completely delocalized (canonical) molecular orbital ϕ . From this we calculate the corresponding Coulomb matrix element $J_{\phi\phi}$ and take the limit for large inter-fragment distances R setting all mixed densities

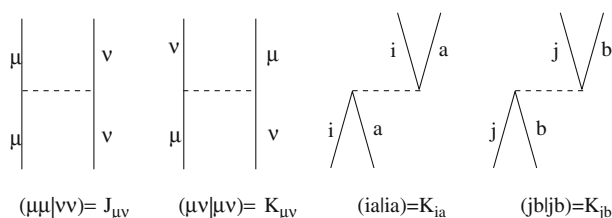


Fig. 3 The matrix elements of the same-index interactions. Possible denominators and signs are not shown since they depend on the rest of the complete diagram

$s_1(\vec{r})s_2(\vec{r})$ to zero:

$$\phi(\vec{r}) = \frac{1}{\sqrt{2}} (s_1(\vec{r}) + s_2(\vec{r})).$$

$$\begin{aligned} J_{\phi\phi} &= (\phi\phi|\phi\phi) \approx \frac{1}{4} [J_{s_1} + J_{s_2} + 2J_{s_1s_2}] \\ &= \frac{1}{2} \left[J_s + \frac{1}{R} \right]. \end{aligned} \quad (10)$$

The result of this elementary consideration is a factor of 2 and an artificial $1/R$ dependence of the correlation energy in canonical orbitals, which is completely absent for perfectly localized orbitals [25]. In practice, this ideal localization can never be achieved and a little effect remains, as we will show in the next section. The dressings introduced above do not change significantly this general result.

Thus there is a fundamental difference between Epstein–Nesbet perturbation theory in localized or in canonical orbitals. In Møller–Plesset perturbation theory the advantage of using localized orbitals remains from a physical point of view only of limited interest since only second-order diagrams in the bi-electronic interactions are summed over. In Epstein–Nesbet theory, however, we deal with infinite summations either over completely dispersed contributions, again without interest, or, in localized orbitals, over the leading contributions to infinite order, damped through the addition of the highly excited EPV diagrams. Trying thus to reproduce the (dressed) Epstein–Nesbet result of canonical orbitals cannot be our concern since the correlation energy becomes distance dependent and as well strongly dependent on the number of atoms, over which molecular orbitals are delocalized.

On the contrary, we would like to use the correlation calculation in the limit of localized orbitals and compete with more sophisticated methods like Coupled-Cluster expansions, but at significantly reduced costs.

The approximation we propose here is a balance between neglecting on one hand attractive contributions of Fock-matrix elements through the use of the difference MP2C – MP2L, and on the other hand neglecting repulsive bi-electronic interactions through the diagonal approximation of the CEPA equations.

Our general working scheme for exploiting the presented theoretical framework for a fairly good and not too expensive estimation of the correlation energy will be the following:

- We produce localized and canonical orbitals for the system to be studied;

- The impact of the off-diagonal Fock-matrix elements will be estimated from the difference of the MP2 energies for canonical and localized orbitals;
- The self-consistently dressed Epstein–Nesbet perturbation contributions will be calculated in localized orbitals.

Before giving numerical results the “experimental” system will be presented briefly.

3 Computational details

For the calculations to be presented, a NH_3 dimer in C_s symmetry is used, one hydrogen atom lying on the line connecting the two nitrogen nuclei.

The basis sets are a $8s5p3d$ basis on nitrogen and a $4s2p$ basis on hydrogen atoms, which are not standard ones, but have been optimized and used for intermolecular problems by Voisin [26,27], starting from a $12s7p$ primitive basis of van Duijneveldt [28] (6s for H), contracted into a $7s4p$ or $3s$ basis, augmented by one diffuse function for each angular momentum, and 3 polarization functions (d functions with five components) for N and 2 p functions on H. The quality has been tested on both monomers and dimer properties [26,27].

For the perturbation calculations mono- and bi-electronic integrals are calculated by the Dalton program package [29]. Generating the SCF wave function, the four-index transformation and the correlation calculations are performed by a (yet unpublished) suite of *ab-initio* programs, which were originally designed for periodic systems, and which have been adapted to dimer systems. All other calculations (CCSD(T), DFT, SAPT) were performed with MOLPRO [30], version 2002.7 and the Delaware SAPT programs [31]; all calculations have been performed on LINUX PCs (Pentium III, RedHat Linux 7.3).

4 Numerical results

In order to obtain localized orbitals for the monomers and the dimer, we could use the well-established localization procedures like that of Foster and Boys [32] or of Pipek and Mezey [33], for each of the systems independently. Doing so, however, leaves us only little control over the shape of the orbitals, and monomer and dimer orbitals may lose their resemblance. This last detail will become important when discussing the Basis Set Superposition Error in the next section.

4.1 Calculating the correlation energy for the dimer

So for the dimer system we chose for an alternative, denoted CIS (Configuration Interaction of Single excitations) in the following: we first calculate the monomer wavefunctions in their respective basis sets through the standard Hartree–Fock procedure, leading to canonical monomer orbitals.

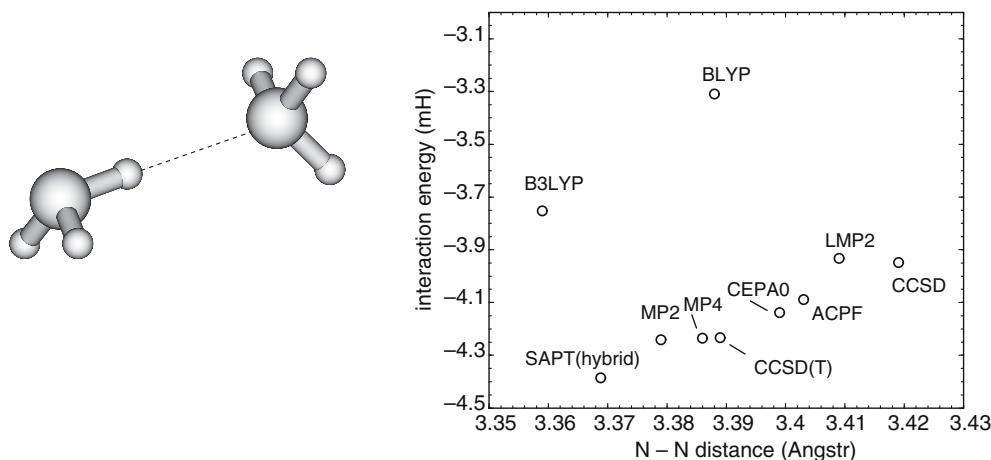


Fig. 4 The ammoniac dimer (*left*) The system is of C_s symmetry, with N–H distances of 1.017 Å and an intra-molecular H–N–H bond angle of 107.81°. The intermolecular N–H–N angle is 180°. On the *right-hand* side we show several typical results for the position and the depth of the intermolecular potential minimum, calculate with different methods, in Ångström and milli-Hartree (1 H = 1 a.u. = 627.51 kcal/mol). The hybrid version of Symmetry-Adapted Perturbation Theory (SAPT) takes the Hartree–Fock intermolecular potential and adds to this correlation corrections obtained from the unperturbed monomer Hartree-Fock wave functions. BLYP and B3LYP are density functional results, whereas LMP2 stands for canonical MP2 perturbation theory, expressed in localized orbitals with non-orthogonal virtual orbitals [30]. Note the relative importance of triple excitations in Coupled-Cluster theory

Table 1 Calculated correlation energies, for the dimer at a N–N distance of 3.000 Å

	MP2L	EN2L(F)	Appr. ACPF	Appr. SCSC
Canonical	−0.470275 (100.0)	−0.513718	−0.505705	−0.495812 (96.9)
CIS	−0.455244 (96.8)	−0.530565	−0.522569	−0.513305 (100.3)
CIS (F)	−0.460619 (97.9)	−0.531611	−0.523252	−0.513497 (100.3)
Pipek–Mezey	−0.424812 (90.3)	−0.526506	−0.520700	−0.514934 (100.6)
Pipek–Mezey (F)	−0.463163 (98.5)	−0.529634	−0.521279	−0.511513 (99.9)
Boys	−0.336275 (71.5)	−0.525607	−0.522455	−0.519038 (101.4)
Boys (F)	−0.465726 (99.0)	−0.534093	−0.525261	−0.514971 (100.6)

The corresponding CCSD(T) result is -0.511835 a.u.. For the (SC)²CI dressing we give the percentage of the CCSD(T) correlation energy in parentheses, for MP2L the percentage of canonical MP2. The diagonalization of F within the orbital spaces attributed to the monomers is indicated by “(F)”. For the Boys and Pipek–Mezey localizations, occupied and virtual orbitals are localized separately, freezing the canonical 1s orbitals on the nitrogen atoms and the twelve highest virtual orbitals. We may remark that even for the Boys localization, which leads to large contributions of the off-diagonal Fock matrix elements, the obtained difference to the CCSD(T) results is only of 1.5% for the (SC)²CI dressing

These orbitals, delocalized over the individual NH₃ monomers, serve as starting orbitals for the occupied and the virtual orbitals of the dimer system, and we iterate now on the sequence of orthogonalization of the occupied orbitals, construction of a Fock matrix, and a CI of mono-excitations, for which the interactions of mono-excited determinants is approximated by the necessary Fock matrix elements, neglecting pure bi-electronic interactions [34,35]. The CI expansion with coefficients c_i^a is projected in first order on a single determinant with corrected occupied (φ_i) and virtual (φ_a) orbitals through

$$\varphi_i \rightarrow \varphi_i + \sum_a c_i^a \varphi_a \quad \text{and} \quad \varphi_a \rightarrow \varphi_a - \sum_i c_i^a \varphi_i. \quad (11)$$

The CI procedure lowers the total energy and assures thus a convergence toward the Hartree–Fock solution of the dimer system. The convergence criterion is in this case Brillouin’s theorem, that is the smallness of Fock-matrix elements coupling occupied and virtual orbitals and the resulting orbitals should represent as most as possible the starting monomer

orbitals. We may even introduce an additional monomer delocalization, in that off-diagonal intra-molecular Fock matrix elements are transformed to zero through a partial diagonalization of the Fock matrix of the dimer system, sketched in Fig. 5. We will denote this monomer delocalization by adding “(F)” to CIS. Diagonalizing the whole Fock matrix in one additional step produces, of course, canonical orbitals.

So we know how to compute the dimer’s Hartree–Fock and correlation energies, in canonical and in localized orbitals. We give in Table 1 the values at $R_{N-N} = 3.00$ Å in detail, for different sets of orbitals. We see that the elimination of intra-molecular non-zero off-diagonal Fock matrix elements approaches the MP2 values for localized orbitals to those of the canonical orbitals, but without changing the results significantly for the dressed Epstein–Nesbet procedure. The importance of avoiding intermolecular delocalization, much more than intramolecular delocalization, is clearly visible when comparing the dressed and undressed Epstein–Nesbet variants for canonical orbitals and the different localized orbital sets.

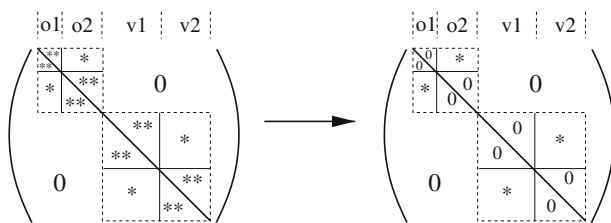


Fig. 5 The diagonalization of the Fock matrix on the monomers. o1 and o2 stand for the occupied orbitals on the two monomers, and v1 and v2 represent the space of the virtual orbitals

The same can be seen in Fig. 6, where we plot the correlation energies as functions of the intermolecular distance. The dressings alone do not result into a correct dependence upon the distance for canonical orbitals, as shown in the left panel of the figure.

For localized orbitals (right panel) we remark first an increase in the MP2 correlation energy with increasing intermolecular distance, due to the decreasing importance of off-diagonal Fock matrix elements. Adding the series of bielectronic interactions through the F-corrected Epstein–Nesbet perturbation (EN2L(F) if not dressed, or approximated ACPF and approximated (SC)²CI with dressing) restores the same trend as MP2 or CCSD(T) with canonical orbitals. We see additionally that including the EPV diagrams through the (SC)²CI dressing, not only the values are closer to the CCSD(T) values but also the variation of results for EN2L(F) of about 0.01 a.u. are reduced by a factor of 2.

Our chosen balance of an approximate inclusion of off-diagonal non-zero Fock matrix elements and EPV diagrams on the infinite series of same-index interactions seems satisfactory for this dimer case, and we may expect the same behaviour for more extended systems.

4.2 The problem of the BSSE correction

For obtaining now an intermolecular potential curve we have to subtract the monomer's total energies. But what orbitals should we take for the monomers? Canonical orbitals seem adequate, since first we started the CIS procedure for the dimer from canonical monomer orbitals and, secondly, we diagonalized the Fock matrix on the monomers. However, in order to correct for the BSSE we should carry out the calculations of the monomers in the full dimer basis [12,36]. Canonical orbitals in this basis diagonalize the Fock matrix in the whole space of the virtual orbitals on both monomers, not only the blocks on each monomer as in Fig. 5, so the question which orbitals to take, is shifted toward the discussion which virtual orbitals to take. There are several possibilities: either we use all canonical orbitals for one monomer, expressed in the monomer basis, and orthogonalize the other monomer's AO space to these orbitals through projection (or Gram–Schmidt orthogonalization) or via the symmetric Löwdin $\mathbf{S}^{-1/2}$ orthogonalization.

Again the CIS procedure relaxes the occupied and virtual orbitals of the monomer toward the Hartree–Fock solution in the complete dimer basis. We may again diagonalize the

Fock matrix on the monomer MO spaces, leaving thus non-zero off-diagonal matrix elements between virtual orbitals on the monomer and the ghost orbitals.

We may use as well another idea: we may start the CIS procedure from the localized molecular orbitals of the complete dimer set, just by reattributing the occupation numbers. The choice of the orthogonalization procedure to generate the virtual space of the ghost orbitals becomes irrelevant since the dimer orbitals form already an orthogonal set. This last variant should produce monomer orbitals which resemble the most to the dimer orbitals. Projection via the Gram–Schmidt procedure and the subsequent relaxation toward the monomer Hartree–Fock solution should give on the other hand the most localized orbitals in the sense that the difference between the calculation with or without the ghost basis should be small.

For the different monomer orbital sets proposed we calculate the correlation energy with our dressed Epstein–Nesbet procedure taking into account the difference between MP2C and MP2L as infinite summation of interactions through off-diagonal Fock-matrix elements. The result for the correlation energies is given for one intermolecular distance in detail in Table 2.

If we compare just the first two lines of Table 2 with canonical orbitals, we find the behavior described in the theoretical considerations. The MP2 energy lowers when augmenting the basis sets, whereas the (dressed) Epstein–Nesbet energies become less important with larger basis sets due to the orbital delocalization over the two monomers. An interesting and a bit unexpected effect arrives when using the different sets of localized orbitals: the only set, for which the correlation energy becomes larger is that generated by orthogonalizing the ghost basis set by the Gram–Schmidt procedure. All other procedures show the same trend of smaller correlation energies for the dressed Epstein–Nesbet results in the dimer basis than in the pure monomer basis.

The lowering of the correlation energy when adding the ghost basis set through the Gram–Schmidt procedure may be expected, since the monomer orbitals are only slightly modified via the subsequent CIS procedure, and all added terms of the form

$$-\langle \Phi_I | \mathbf{V} | \Phi_0 \rangle^2 / \langle \Phi_I | \mathbf{H} - E_{\text{HF}} | \Phi_I \rangle$$

are negative. For the other orbital sets the added terms remain negative, but the original terms may have changed due to the orbital deformation by orthogonalization to less negative values and thus an overall decrease in the correlation energy occurs. By the way we found through the Gram–Schmidt procedure an example, where the infinite series of Fock-matrix elements (Fig. 2) gives a positive (repulsive) energy contribution, i.e., the MP2L energy is lower than the MP2 energy in canonical orbitals.

We may advance two arguments for choosing a construction of monomer orbitals to be used to calculate an interaction energy. For the orbitals obtained through orthogonalization, we started from the same sets for monomer and for dimer orbitals, namely canonical monomer orbitals in the basis sets of the respective monomers. But on the other hand, the closest

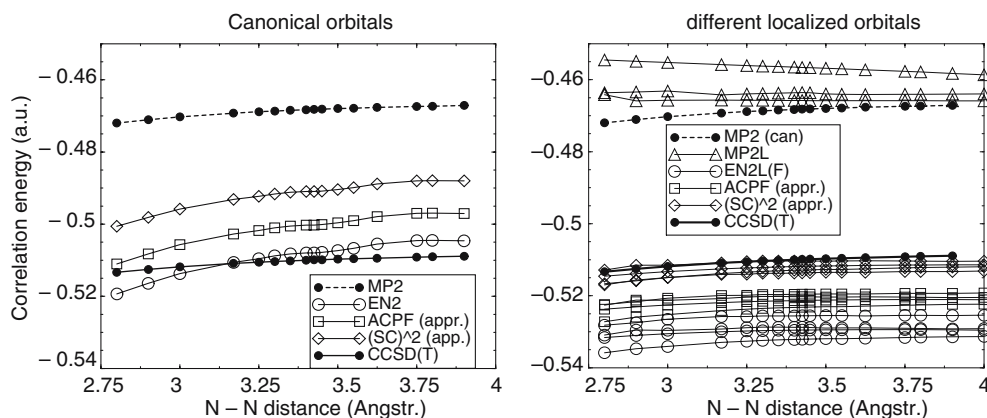


Fig. 6 Correlation energies for the dimer system. The *left panel* shows the different Epstein–Nesbet variants in comparison to MP2 and CCSD(T), all in canonical orbitals. The wrong dependence on the intermolecular distance of the Epstein–Nesbet scheme is clearly visible. The *right panel* shows the same variants for different sets of localized orbitals (Pipek–Mezey localization, Pipek–Mezey localization with diagonalization of \mathbf{F} on the monomers, localization via the CIS scheme (see text), both with and without diagonalization of \mathbf{F} on the monomers)

Table 2 Sum of the two monomer correlation energies, at a N–N distance of 3.000 Å

	MP2L	EN2L(F)	ACPF(approx.)	(SC) ² (approx.)
Monomer basis				
Canonical	−0.466007	−0.531440	−0.522287	−0.511821
Dimer basis				
Canonical	−0.467137	−0.509344	−0.501588	−0.492834
CIS with projection	−0.467859	−0.532708	−0.523496	−0.513305
CIS with $\mathbf{S}^{-1/2}$	−0.453774	−0.528116	−0.520054	−0.510832
The same with diag F	−0.462438	−0.528561	−0.520013	−0.510172
CIS from dimer CIS(F)	−0.447605	−0.525644	−0.518076	−0.509429
The same with diag F	−0.451887	−0.526343	−0.518485	−0.509457

Different sets of orbitals are employed. The corresponding CCSD(T) results are −0.508877 a.u. (monomers in the dimer basis) and −0.507724 a.u. (monomers in their respective basis). For “CIS” see text

resemblance between monomer and dimer orbitals, and thus the best account for the presence of the dimer basis set for both the monomer and dimer calculations should be obtained when recalculating monomer orbitals with the dimer orbitals as starting point. This procedure seems to us the most balanced approach for calculating the interaction energy, relying on the three-step procedure

1. Determine a set of canonical monomer orbitals in the respective monomer AO basis sets,
2. Calculate dimer orbitals through the CIS or CIS(F) procedure from the monomer orbitals,
3. Take the CIS or CIS(F) orbitals as starting vectors to obtain monomer orbitals in the dimer basis

and avoiding an additional arbitrariness through the choice of the orthogonalization procedure (Gram–Schmidt or $\mathbf{S}^{-1/2}$ or others). In this way the orbital delocalization – which may be suspected to be present in the dimer calculation as well when approaching the two monomers – is taken into account for both the dimer and the monomer system and we may hope to achieve a consistent correction for the basis set superposition error.

Thus we may accept this *a priori* unusual behavior of the correlation energy for the monomer systems: we augment

Table 3 Minima of the intermolecular interaction potential for the NH₃ dimer, in mH and in kcal/mol

	R (Å)	ΔE (mH)	ΔE (kcal/mol)
CCSD(T)	3.389	−4.23	−2.66
MP2C	3.379	−4.21	−2.65
CIS, appr. (SC) ² CI	3.330	−4.66	−2.92
CIS, appr. ACPF	3.308	−5.09	−3.19

the basis set and the perturbative correlation energy becomes smaller.

The fact that the orbital delocalization plays a rôle as well for the dimer system, may be seen when we plot the correlation energy for different intermolecular distances in a smaller scale than that used in Fig. 6.

Figure 7 displays the correlation energies for the approximated (SC)² in comparison to CCSD(T) and MP2, for the monomer and dimer separated, and the contribution to the potential energy curve, to be added to the Hartree–Fock interaction energy. The monomer orbitals are those obtained from the CIS procedure, without diagonalization of the Fock matrix on the monomers.

We clearly see the unusual behavior of the EN perturbative correlation energy for the monomers from the left

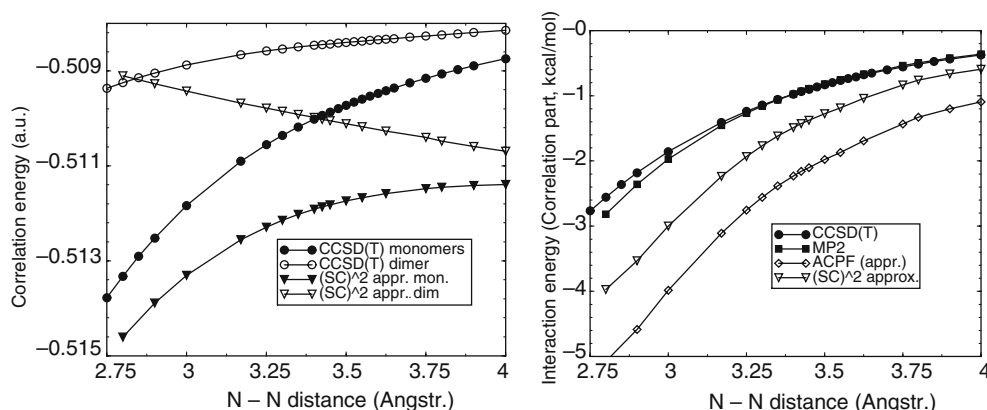


Fig. 7 The correlation contributions to the interaction potential. On the left-hand side the individual contributions for monomers and the dimer are plotted, and on the right-hand side their difference, which is added to the Hartree–Fock interaction energy

panel: we approach the ghost basis sets and the correlation energy decreases in value. However, this “anti-BSSE” behavior seems well compensated when comparing the dimer curves, where for short distances the $(SC)^2$ -dressed Epstein–Nesbet perturbation approaches the CCSD(T) values more than for larger distances. The difference between dimer and monomers, i.e., the correlation contribution to the interaction energy, results therefore in a converging picture, when comparing MP2/CCSD(T) and the $(SC)^2$ dressed Epstein–Nesbet energies. The ACPF dressing seems to produce a systematic error. Of course we remark that the simple MP2 scheme gives a much better coincidence with CCSD(T) than our proposed dressed Epstein–Nesbet theory, where we obtain deviations from the CCSD(T) results up to 1 kcal/mol. Nevertheless, the often cited “lack of size consistence” defect of Epstein–Nesbet perturbation theory may be expected to be controlled through the combination of localization, dressing and inclusion of the off-diagonal Fock-matrix elements. Of course, a rigorous proof still has to be furnished.

When adding the Hartree–Fock interaction energy and the correlation contributions into a single intermolecular interaction potential, which we show in Fig. 8, we obtain a

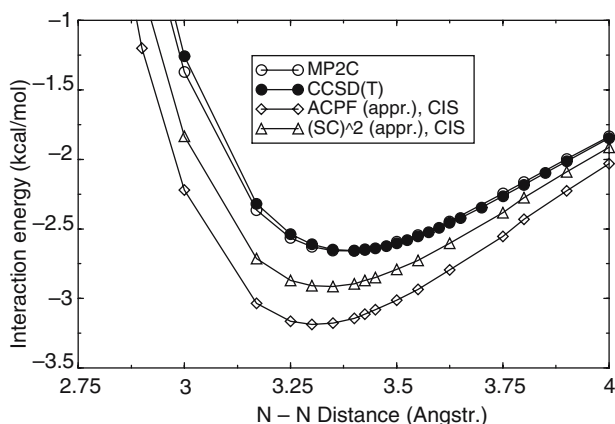


Fig. 8 The intermolecular potential, compared to CCSD(T)

minimum of the potential close to the MP2/CCSD(T) values, in the order of half a kcal/mol and an equilibrium distance 5 pm off from the reference values. It may be useful to recall that the initial development of this method was not the calculation of an interaction energy, but rather the efficient calculation of a correlation energy through perturbation theory. The application to weakly interacting dimer system presents a quite difficult situation for a method being in general not size consistent and not invariant to orbital rotations.

5 Conclusion

We showed that combining the Epstein–Nesbet second-order perturbation theory with infinite summations of EPV diagrams and infinite summations of off-diagonal Fock matrix elements leads to an approximation of CEPA-based correlation methods and produces correlation energies comparable to CCSD(T) results for extended systems, at much lower cost. The dependence on the shape of the orbitals or on the localization procedure is strongly damped with respect to simple second-order Epstein–Nesbet perturbation theory, through the inclusion of both (1) an approximate treatment of the non-zero off-diagonal Fock matrix elements and (2) a diagonal matrix dressing to account for the infinite summations of EPV diagrams, which are accessible without extra significant effort.

Using the procedure with localized orbitals avoids the two defects of Epstein–Nesbet perturbation due to complete delocalization of canonical orbitals: the artificial $1/R$ contribution to the correlation energy and the wrong dependence on the number of particles in the system.

However, a critical test of the dressed Epstein–Nesbet procedure, the calculation of the intermolecular interaction energy of a NH_3 dimer, showed that orbital delocalization due to the implication of ghost basis sets is very delicate when calculating the monomer’s correlation energies and makes reliable estimates of small energy differences difficult. Looking at correlation energies of the monomers only, we still see an unexpected behavior due to orbital delocalization on the

ghost functions. In the dimer AO basis, the EN monomer perturbative correlation energies decrease with decreasing intermolecular distance. We propose a three-step construction of dimer and monomer orbital sets which seems to take this unexpected “anti-BSSE” effect in a balanced way into account and leads to reasonable interaction energies for the NH₃ dimer studied.

Thus we conclude that the proposed dressed Epstein–Nesbet perturbation theory with localized orbitals may be a good alternative to current trends to calculate correlation energies for periodic systems – this still has to be confirmed – but should not be employed for intermolecular interactions. For these systems the simple second-order Møller–Plesset perturbation theory in canonical orbitals remains a method of choice due to the very effective cancellation of missing correlation diagrams for monomer and dimer correlation energies

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