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Possible Artifacts Occurring in the Calculation of Intermolecular Energies from Delocalized Pictures

J. P. Malrieu and F. Spiegelmann

Laboratoire de Physique Quantique, Université Paul Sabatier, 118, route de Narbonne, F-31077 Toulouse Cedex, France

The intermolecular energy between two identical subsystems may be calculated from symmetry *delocalized* MO's resulting for instance from a preliminary SCF calculation of the supersystem. Then each second-order energy correction mixes intramolecular correlation, R^{-6} intermolecular dispersion energy, and R^{-3} components. The R^{-3} components disappear through subtle cancellations. The shifted Epstein-Nesbet energy denominators introduce an artificial second-order intermolecular R^{-1} component, which would be cancelled by off-diagonal third-order terms, as well as a bad asymptotic limit at infinite distances. The R^{-1} artifact will also occur in strong symmetrical chemical bonds calculated in the Epstein-Nesbet perturbation scheme from delocalized MO's. These defects will occur in all variational approximate CI techniques which neglect off-diagonal elements between delocalized doubly excited determinants. These artifacts are avoided when using the Moller-Plesset definition of the zeroth order Hamiltonian or when starting from (SCF) *localized* MO's (even in the Epstein-Nesbet perturbation). The discussion is exemplified on an accurate *ab initio* calculation of the Ar_2 molecule.

Key words: Delocalized MOs

1. Introduction

The *ab initio* calculation of Van der Waals intermolecular dispersion energies is not easy. The connection between the long range perturbative treatment of intermolecular forces [1] and the short range repulsive region was difficult to establish in a clear way [2]. Practical approaches have now been proposed to solve this problem (for a review see Ref. [3]). All of them start from localized descriptions of the subsystem, starting either from the properly orthogonalized SCF MO's of the isolated molecules [4] or from the localized SCF MO's of the supermolecule [5–9].

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It may seem rather strange to start from symmetry adapted MO's of the supersystem in symmetric intermolecular problem, such as a homonuclear diatomic problem, since each MO is then spread over both systems, preventing the useful partition of the correlation corrections into *intra* and *inter* molecular contributions. In some cases, for instance in excited states studies, the use of symmetry MO's may be recommended, and the purpose of this paper is to analyze the behaviour of intramolecular and intermolecular contributions when they are hidden under symmetry corrections.

2. Perturbation Expansions, Concepts and Illustrative Results

Let us consider two identical subsystems A and B. Let us define a set of SCF MO's for each of them $\{\varphi_i^{a,b}\}$. A proper orthogonalization of these MO's will lead to a set of localized MO's

$$\varphi_i'^{a,b} \simeq \varphi_i^{a,b}(1 + \mathcal{O}(s^2))$$

which only differ from the original SCF MO's through overlap second order effects. Associating two by two these localized MO's one gets symmetry adapted MO's for the supersystem

$$\varphi_{i+} = (\varphi_i'^a + \varphi_i'^b)/\sqrt{2},$$

$$\varphi_{i-} = (\varphi_i'^a - \varphi_i'^b)/\sqrt{2}.$$

The same transformation would be possible for the virtual MO's. The ground state determinant

$$\begin{aligned}\phi^{0(\mathrm{A+B})} &= \mathscr{A}\prod_{i=1}^{N} \varphi_i'^a\varphi_i'^b \\ &= \mathscr{A}\prod_{i=1}^{N} \varphi_{i+}\varphi_{i-}\end{aligned}$$

already contains the repulsive and electrostatic energy components. If an SCF adjustment of the supermolecule MO's has been performed it also gives the polarization and charge transfer corrections. Perturbing the $\phi^{0(\mathrm{A+B})}$ zeroth order wave function will give *intra* and *inter* molecular correlation effect. One may recall the various perturbation expansions generally used in the correlation problem. The Brillouin-Wigner perturbation is known to give an unsatisfactory N dependence [10]. In the Rayleigh-Schrödinger expansion, two partitions of the total Hamiltonian are generally used [11].

In the Moller-Plesset definition [12], the H_0 Hamiltonian is the sum of Hartree-Fock monoelectronic operators. If the ε_i's are the diagonal Fock operator elements for all MO's

$$H_0 = \sum_i \varepsilon_i a_i'^a a_i + C.$$

In this partition the energy denominators always are differences between the holes and particles Fock energies. The linked cluster theorem is demonstrated in this definition of H_0.

The Epstein-Nesbet definition [13, 14] of H_0 consists in partitioning the total Hamiltonian into a diagonal H_0 and a non-diagonal V operator. If I is a typical determinant of the CI basis set

$$H_0|I\rangle = \langle I|H|I\rangle|I\rangle \qquad H_0 = \sum_I \langle I|H|I\rangle|I\rangle\langle I|$$

$$\langle I|V|J\rangle = \langle I|H|J\rangle(1 - \delta_{IJ}).$$

The energy denominators are then "shifted" energy denominators

$$\langle O|H_0|O\rangle - \langle I|H_0|I\rangle = \langle O|H|O\rangle - \langle I|H|I\rangle.$$

Both partitions may be used either on localized or delocalized MO's. The localized picture is the most logical for intermolecular problems. The intramolecular double excitations

$$|I\rangle = \left|\begin{matrix} j_a^* & l_a^* \\ i_a & k_a \end{matrix}\right\rangle$$

give most of the intramolecular correlation corrections at the second-order level, while the intermolecular double excitation, which are simultaneous single excitations on both subsystems

$$|I\rangle = \left|\begin{matrix} j^* & l^* \\ i_a & k_b \end{matrix}\right\rangle$$

lead to the Van der Waals dispersion forces. This approach may be used in numerical calculations, sometimes only considering the second class of excitations [5, 6], sometimes considering simultaneously intra and inter double excitations [8, 9].

While we were involved in excited states studies of the Ar_2 dimer, a ground state calculation was performed using symmetry adapated MO's in a rather large basis set [15]. The core electrons were represented through a non-empirical pseudopotential determined according to the Barthelat and Durand method [16]. Fig. 1 represents the Hartree-Fock and second-order corrected energy variations in both definitions of H_0, while the experimental well depth is about 100 cm^{-1} at 7.2 a.u. [17]. These results are also reported in Table 1 with, in the last column, twice the calculated energy of an isolated argon atom. Our purpose is not to discuss the slight discrepancy between experiment and our 2nd order MPRS result, which may result from the so-called "basis set extension effect" [18], artificially stabilizing the intermolecular situations by offering to the electrons of an atom a possible delocalization in the virtual MO's of its partner. The points under discussion here are:

the huge discrepancy of the Epstein-Nesbet 2nd order result, for which the well depth is exaggerated by one order of magnitude,

the bad convergence of this Epstein-Nesbet molecular energy towards the sum of the energies of two isolated atoms.

The next section offers an explanation of these phenomenons and shows that both derive from shifted Epstein-Nesbet denominators.

Table 1. Energies of the ground state of the Ar_2 dimer calculated with the Epstein–Nesbet and Moller–Plesset partitions

R (a.u.)	4	5	6	7	8	9	Atom (×2)
E.N. (a.u.)	−41.647635	−41.751407	−41.764061	−41.762545	−41.759907	−41.757760	−41.824259
M.P. (a.u.)	−41.577563	−41.686617	−41.703354	−41.704915	−41.704662	−41.704415	−41.703922

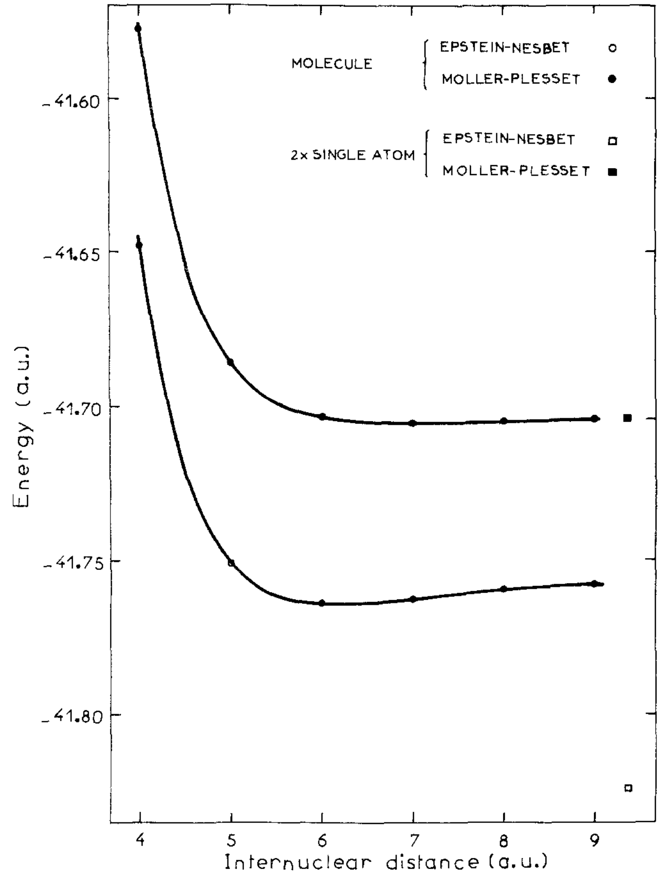


Fig. 1. Interatomic potential curves for the Ar_2 problem (non-empirical pseudopotential, after a 2nd order Rayleigh-Schrödinger calculation, see Ref. [15])

3. The M.P. and E.N. 2nd Order Results for the He_2 Problem

In order to simplify our problem, let us consider two He atoms, at such a distance that the interatomic overlap may be neglected. The interatomic problem will be treated simultaneously in the equivalent delocalized symmetry adapted and localized representations. The MO's may eventually be distorted through polarization effects. The set of localized MO's, s_a, s_b, is equivalent to the σ_g, σ_u set

$$\begin{bmatrix} \sigma_g = (s_a + s_b)/\sqrt{2} \\ \sigma_u = (s_a - s_b)/\sqrt{2} \end{bmatrix} \equiv \begin{bmatrix} s_a \\ s_b \end{bmatrix}, \qquad \phi_0 = |\sigma_g\bar{\sigma}_g\sigma_u\bar{\sigma}_u| = \pm\,|s_a\bar{s}_a s_b\bar{s}_b|.$$

As a typical correlation effect we shall consider the correlation involving the $2p$ AO's. For the sake of simplicity we only introduce one set (for instance $2p_x$) of these AO's. The same transformation is possible for these virtual MO's

$$\begin{bmatrix} \pi_g = (2p_a - 2p_b)/\sqrt{2} \\ \pi_u = (2p_a + 2p_b)/\sqrt{2} \end{bmatrix} \equiv \begin{bmatrix} 2p_a \\ 2p_b \end{bmatrix}.$$

It is well known that the subspace of the doubly excited state is stable under any unitary transformation of the occupied MO's among themselves and under such a transformation among the virtual MO's. Therefore if the doubly excited states built from delocalized (resp. localized) MO's are labelled $|I\rangle$ (resp. $|I'\rangle$),

$$\sum_I{}' |I\rangle\langle I| = \sum_{I'}{}' |I'\rangle\langle I'|$$

hence

$$\sum_I{}' \langle O|H|I\rangle\langle I|H|O\rangle = \sum_{I'}{}' \langle O|H|I'\rangle\langle I'|H|O\rangle.$$

One recognizes here the numerators of the second-order energy corrections and therefore a difference between the localized and delocalized pictures in a given definition of the perturbation expansion may only result from the energy denominators. Regarding these energy denominators, the neglect of intermolecular overlap implies a strict degeneracy of the Fock operator

$$\varepsilon_{\sigma_g} = \varepsilon_{\sigma_u} = \varepsilon_{s_a} = \varepsilon_{s_b} = \varepsilon$$

$$\varepsilon_{\pi_g} = \varepsilon_{\pi_u} = \varepsilon_{2p_a} = \varepsilon_{2p_b} = \varepsilon'.$$

In such a case, all the energy denominators of the Moller-Plesset partition are identical

$$\langle O|H_0|O\rangle - \langle I|H_0|I\rangle = \langle O'|H_0|O'\rangle - \langle I'|H_0|I'\rangle = 2(\varepsilon - \varepsilon') \; \forall \; I, I'.$$

It is therefore evident that the Moller-Plesset result is independent on the localization of the MO's. This is a special case of a well known result; the M.P. expansion is stable under any unitary transformation within the degenerate sets of MO's, as directly seen from its explicit expression.

3.1. Appearance and Disappearance of R^{-3} Terms in the Delocalized Picture

It may be interesting to see the way by which such an invariance is obtained. In our simplified problem, ten doubly excited determinants have to be considered in the symmetry-adapted representation, the interaction of which with $|O\rangle$ is given

$$|I\rangle = \left\{\begin{array}{ll}
(\sigma_g \to \pi_g)^2 & \langle O|H|I\rangle = K_{\sigma_g\pi_g} = (K_{s_ap_a} - (s_ap_a, s_bp_b))/2 \\
(\sigma_u \to \pi_u)^2 & \qquad\qquad\;\; = K_{\sigma_u\pi_u} = (K - a/R^3)/2 \\
(\sigma_u \to \pi_g)^2 & \qquad\qquad\;\; = K_{\sigma_u\pi_g} = (K + a/R^3)/2 \\
(\sigma_g \to \pi_u)^2 & \qquad\qquad\;\; = K_{\sigma_g\pi_u} = (K + a/R^3)/2 \\
\left.\begin{array}{l}(\sigma_g\sigma_u \to \pi_g\pi_u)\\ (\bar\sigma_g\bar\sigma_u \to \bar\pi_g\bar\pi_u)\end{array}\right\} & \langle O|H|I\rangle = (\sigma_g\pi_g, \sigma_u\pi_u) - (\sigma_g\pi_u, \sigma_u\pi_g) = +a/R^3 \\
\left.\begin{array}{l}(\sigma_g\bar\sigma_u \to \pi_g\bar\pi_u)\\ (\bar\sigma_g\sigma_u \to \bar\pi_g\pi_u)\end{array}\right\} & \qquad\qquad\;\; = (\sigma_g\pi_g, \sigma_u\pi_u) = (K - a/R^3)/2 \\
\left.\begin{array}{l}(\sigma_g\bar\sigma_u \to \pi_u\bar\pi_g)\\ (\bar\sigma_g\sigma_u \to \bar\pi_u\pi_g)\end{array}\right\} & \qquad\qquad\;\; = (\sigma_g\pi_u, \sigma_u\pi_g) = (K + a/R^3)/2
\end{array}\right.$$

The previous calculations neglect integrals with asymptotic exponential decreasing behaviour. Summing up the squares of all these numerators, one gets

$2K^2/2(\varepsilon - \varepsilon')$ which gives the intraatomic correlation energy of both atoms,

$4(a/R^3)^2/2(\varepsilon - \varepsilon')$ which gives the R^{-6} Van der Waals interatomic dispersion energy.

This result may be obtained directly in the localized picture since the only interacting doubly excited states are (excluding those giving exponential-like decreasing numerators)

$$|I'\rangle = \left\{\begin{array}{l} \left.\begin{array}{l}(s_a \rightarrow 2p_a)^2\\ (s_b \rightarrow 2p_b)^2\end{array}\right\} \quad \langle O'|H|I'\rangle = K \\ \left.\begin{array}{l}(s_a s_b \rightarrow 2p_a 2p_b)\\ (\bar{s}_a \bar{s}_b \rightarrow 2\bar{p}_a 2\bar{p}_b)\\ (s_a \bar{s}_b \rightarrow 2p_a 2\bar{p}_b)\\ (\bar{s}_a s_b \rightarrow 2\bar{p}_a 2p_b)\end{array}\right\} \langle O'|H|I'\rangle = (s_a p_a, s_b p_b) = a/R^3 \end{array}\right.$$

In the localized description the separation between intra and interatomic contributions is direct, while the delocalized picture mixes them. Every delocalized doubly excited determinant brings a part of intra, and interatomic correlations, plus an R^{-3} artificial component, the sum of which cancels. *The cancellation is obtained only from the summation of* all *determinants; a method which would neglect some of them from energy criteria such as is frequently done in* CI *approximations might introduce these R^{-3} terms.*

3.2. Appearance of R^{-1} Terms in the Epstein-Nesbet Second-Order Energy in the Delocalized Picture

Let us turn now to the change due to the energy shift in the E–N perturbation. For the first excited determinant $|I\rangle = (\sigma_g \rightarrow \pi_g)^2$

$$\langle O|H|O\rangle - \langle I|H|I\rangle = 2(\varepsilon - \varepsilon') + 4J_{\sigma_g\pi_g} - J_{\sigma_g\pi_g} - J_{\pi_g\pi_g} - 2K_{\sigma_g\pi_g}$$

$$J_{\sigma_g\pi_g} = (\sigma_g\sigma_g, \pi_g\pi_g) = (s_a^2 + s_b^2, 2p_a^2 + 2p_b^2)/4 = (J_{s_ap_a} + J_{s_ap_b})/2.$$

The second Coulombic integral may be approximated by $1/R$. In the same way

$$J_{\sigma_g\sigma_g} = \frac{J_{s_as_a} + 1/R}{2}$$

$$J_{\pi_g\pi_g} = \frac{J_{p_ap_a} + 1/R}{2}.$$

While

$$K_{\sigma_g\pi_g} = (\sigma_g\pi_g, \sigma_g\pi_g) = \frac{K_{s_ap_a} - a/R^3}{2}.$$

Therefore

$$\Delta E_{\mathrm{EN}} = 2(\varepsilon - \varepsilon') - J_{s_as_a}/2 - J_{p_ap_a}/2 + 2J_{s_ap_a} - K_{s_ap_a} + 1/R$$

$$\Delta E_{\mathrm{EN}} = 2(\varepsilon - \varepsilon') + C + R^{-1} + O(R^{-2})$$

where C is an intraatomic constant and B another constant since $\sigma_g^2 = \sigma_a^2 = (s_a^2 + s_p^2)/2$ and $\pi_g^2 = \pi_u^2 = (2p_a^2 + 2p_b^2)/2$

$$J_{\sigma_g\pi_u} = J_{\sigma_u\pi_g} = J_{\sigma_u\pi_u} = J_{\sigma_g\pi_g}, \qquad J_{\sigma_u\sigma_u} = J_{\sigma_g\sigma_u} = J_{\sigma_u\sigma_u},$$
$$J_{\pi_g\pi_u} = J_{\pi_g\pi_g} = J_{\pi_u\pi_g}$$

and all the denominator energies for the closed-shell doubly excited determinants are equal. If one neglects the R^{-2} and R^{-3} terms, the denominators relative to the open shell doubly excited determinants have exactly the same expression, except for the $(\sigma_g\sigma_u \rightarrow \pi_g\pi_u)$ and $(\sigma_g\sigma_u \rightarrow \pi_g\pi_u)$ double excitations but then the associated numerators are zero in our approximation, and the Epstein-Nesbet second order correction is therefore equal to

$$\varepsilon_{\text{EN}}^2 = \frac{2K^2}{\Delta E_{\text{eff}}} + \frac{a^2}{R^6\,\Delta E_{\text{eff}}} \quad \text{with} \quad \Delta E_{\text{eff}} = \Delta E_{\text{MP}} + C + R^{-1}$$
$$= (\Delta E_{\text{MP}} + C)(1 + R^{-1}/(\Delta E_{\text{MP}} + C)).$$

$\Delta E_{\text{MP}} + C = 2(\varepsilon - \varepsilon') + C$ is the intraatomic double excitation transition energy for $R = \infty$. Therefore

$$\varepsilon_{\text{EN}}^2 \simeq \frac{2K^2}{\Delta E_{\text{MP}} + C}\left[1 - \frac{R^{-1}}{\Delta E_{\text{MP}} + C} + \mathcal{O}(R^{-2})\right] + \frac{a^2}{R^6(\Delta E_{\text{MP}+C})} + \mathcal{O}(R^{-7}).$$

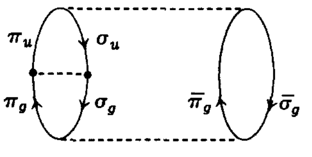
The first term $2K^2/(\Delta E_{\text{MP}} + C)$ is the $(R = \infty)$ intraatomic Epstein-Nesbet 2nd order correlation energy. But it is multiplied by a factor larger than 1 which increases as R^{-1}, leading to an artificial stabilization of the ground state. This artificial R^{-1} component, is clearly due to the ionic components of the doubly excited determinants.

The localized Epstein-Nesbet treatment of our problem would not introduce this R^{-1} component, which is a pure artifact. Of course the MP treatment would introduce this term as a third-order correction involving the diagonal values of the perturbation operator

$$\langle O|H|I\rangle\langle I|V|I\rangle\langle I|H|O\rangle/\Delta E^2.$$

But this third-order contribution would be cancelled by other third order R^{-1} components. It would be too lengthy to show the complete analytical cancellations occurring at the third order among R^{-1} terms. Let us illustrate only the appearance of positive R^{-1} third-order components

$$\frac{\langle O|H|I\rangle\langle I|H|J\rangle\langle J|H|O\rangle}{(E_O - E_I)(E_O - E_J)} \quad I = (\sigma_g \rightarrow \pi_g)^2, \quad J = (\bar{\sigma}_g\sigma_u \rightarrow \bar{\pi}_g\pi_u).$$



$$\langle I|H|J\rangle = -(\pi_g\pi_u, \sigma_g\sigma_u)$$
$$= -(2p_a^2 - 2p_b^2, 2s_a^2 - 2s_p^2)$$
$$= -(J_{s_a2p_a} - R^{-1}).$$

This diagram leads to a repulsive $(K^2/\Delta E^2)R^{-1}$ contribution, partly cancelling the previously noticed R^{-1} attractive component.

3.3. Bad Asymptotic Convergence of the Molecular Energy towards the Atomic Situation with the Epstein-Nesbet Partition

We wrote previously, up to the second order of R^{-1}, the Epstein-Nesbet denominators. At infinite internuclear distance they become:

$$\Delta E_{\mathrm{EN}} = 2(\varepsilon - \varepsilon') - \frac{J_{s_a s_a}}{2} - \frac{J_{p_a p_a}}{2} + 2J_{s_a p_a} - K_{s_a p_a}.$$

And all non-zero numerators are equal to $K^2_{s_a p_a}/4$. Then the Epstein-Nesbet second order asymptotic correction is:

$$\varepsilon^{(2)}_{\mathrm{EN}} = \frac{2K^2_{p_a p_a}}{2(\varepsilon - \varepsilon') + C}$$

Let us come back to the isolated atom. In our model the only double excitation is $(s_a \rightarrow p_a)^2$. Then for one atom

$$\varepsilon^{(2)}_{\mathrm{EN}} = \frac{K^2_{s_a p_a}}{2(\varepsilon - \varepsilon') - J_{s_a s_a} - J_{p_a p_a} + 4J_{s_a s_a} - K_{s_a p_a}}$$

For two atoms, we obtain:

$$\varepsilon^{(2)}_{\mathrm{EN}} = \frac{2K^2_{s_a p_a}}{2(\varepsilon - \varepsilon') + 2C}$$

Then the molecular energy, for large R, does not converge to twice the atomic energy derived with the same treatment, but towards a shifted atomic energy. Of course this artifact does not happen in the Moller-Plesset partition for all denominators are equal. The C constant being positive we can plot the following scheme for the asymptotic situation

———————— $\varepsilon^2_{\mathrm{MP}}$

———————— $\varepsilon^2_{\mathrm{EN}}$ molecular

———————— $\varepsilon^2_{\mathrm{EN}}$ atomic × 2.

4. Discussion

We have plotted on Fig. 2 the R^{-1} dependence of the difference between the Moller-Plesset and Epstein-Nesbet energies. The result is a very good linear fit, as predicted by our simple theory.

The relative positions of our calculated results at infinite internuclear distance are also in agreement with the theoretical conclusions of Sect. 3.3.

This numerical example, enlightened by our brief algebraic derivation on a simplified model problem, allows us to draw a series of conclusions:

1) No problem will arise when the treatment is done as a *localized* representation, whatever the definition of the zeroth order Hamiltonian. This is a supplementary argument in favour of localized pictures, which closely follow the physical *local*

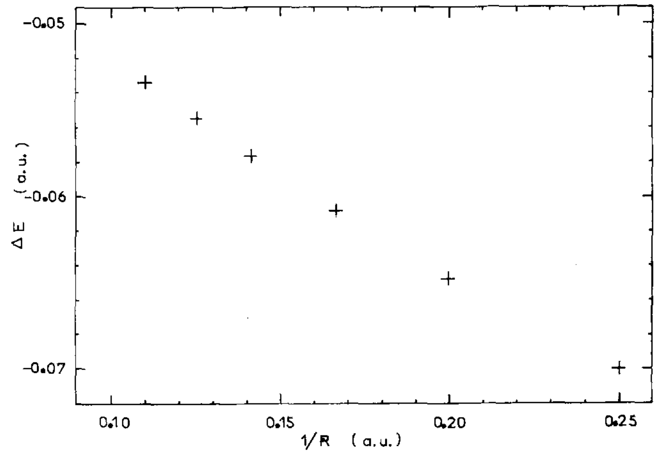


Fig. 2. *R* dependence of the differences between the Moller-Plesset and Epstein-Nesbet 2nd order connections

interactions and avoid, in our case, the R^{-3} components, the R^{-1} behaviour of some "intra" correlation contributions, and the bad asymptotic convergence. For localized pictures the possible superiority [11] of the Epstein-Nesbet partition holds.

2) If one works in a delocalized picture, the Moller-Plesset partition proves to be qualitatively superior to the Epstein-Nesbet one, since it does not introduce the R^{-1} attractive energies which would be cancelled at the 3rd order level and converges to be right atomic limit. This result is related to a well known property of the Moller-Plesset Hamiltonian, namely that it is invariant under unitary transforms of degenerate orbitals, while the Epstein-Nesbet Hamiltonian is not. This fact explains the bad asymptotic convergence, but our analysis holds when the degeneracy between orbitals is split, and is therefore much more general.

As concern the perturbation schemes (Brillouin-Wigner as well as Rayleigh-Schrödinger), the situation may be summarized as follows

	M.P.	E.N.
localized MO's	O.K.	possibly superior
delocalized MO's	O.K. ≡ localized	wrong

3) Our conclusions go far beyond the perturbative procedures, it also concerns the (necessarily approximate) variational CI procedures, as far as they do not allow the cancellation between the R^{-1} diagonal and off-diagonal third-order contributions. Off-diagonal elements are neglected for instance in the A_k and B_k Shavitt's procedures [19]; the hole-hole interactions are neglected in the (IEPA) independent electron pair approximation [20–22], and in practice the neglect of the off-diagonal "tail" elements in Segal *et al.* procedure [23] will lead to the same

defects. Adding independent contributions E_i of the various excited determinants $|I\rangle$ to a previously selected subspace, as handled in the selection and extrapolation procedure of the MRDCI [24] technique, would also introduce this R^{-1} artifact.

4) One may demonstrate that such an effect may occur in excited states studies. This is the reason why our CIPSI calculation of the excited states of the Ar_2 dimer [15] was performed using the Moller-Plesset definition of H_0, while our previous similar studies used the E.N. formalism.

5) This artifact is not limited to intermolecular problems, it should be present in strong molecular bonds as well. Let us consider for instance the F_2 molecule; the lone pairs of the F atoms play the same role as the basic electron pairs of our previously studied model problem. When correlating these electron pairs in a delocalized scheme, they enter symmetrical MO's. For π lone pairs

$$\pi_u = (\pi_1 + \pi_2)/\sqrt{2}$$
$$\pi_g = (\pi_1 - \pi_2)/\sqrt{2}$$

and the double excitations towards vacant MO's built from, let us say, $3p$ AO's will introduce the same R^{-1} artifactual component if they are not handled in a correct fashion, allowing the cancellation between diagonal

$$\langle O|V|I\rangle\langle I|V|I\rangle\langle I|V|O\rangle/\Delta E_I^2$$

and off-diagonal

$$\langle O|V|I\rangle\langle I|V|J\rangle\langle J|V|O\rangle/\Delta E_I\Delta E_J$$

third order corrections. These R^{-1} artifacts may be smaller than the resonance interactions which build the deep hole of an actual chemical bond, but they may be present and significantly lower the energy minimum and bond distance.

One may notice that the above discussed problem no longer holds for unsymmetrical intermolecular problems since their canonical MO's tend to be localized.

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