

SEMIEMPIRICAL EPCE-F2 σ CORRELATION ENERGIES FOR VAN DER WAALS COMPLEXES AND ENERGIES OF REACTION

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Van der Waals complexes are demonstrated to be a field in which the use of the semiempirical EPCE-F2 σ method is justifiable. The systems treated are H₂...H₂O, H₂...HF, HF...HF, H₂O...H₂O, H₂O...F⁻ and C₂H₄...C₂H₄. The EPCE-F2 σ results are judged against the results of reported nonempirical treatments and the merits and limits of the method are discussed.

Previously it has been shown that the predictions given by *ab initio* SCF calculations for many chemically interesting quantities, such as binding energies¹, ionization potentials^{2,3} and excitation energies³, may be improved if the correlation energy is semiempirically accounted for by means of the effective pair correlation energy (EPCE) approximation. In this paper we try to specify application limits of such an approach for energy predictions and to demonstrate van der Waals interactions as a field in which the use of the EPCE approach may be profitable. It is hoped that the results presented in this paper will help to establish the cases, where the EPCE approximation may be expected to give reliable semiquantitative predictions for larger molecules for which a more sophisticated treatment is not feasible.

CALCULATIONS

Use was made of the semiempirical effective pair correlation energy method with the F2 σ approximation (EPCE-F2 σ method) and the parameter set *C* (for details see refs^{4,5}). Electron densities and two-centre effective pair correlation energies appearing in the EPCE-F2 σ formula

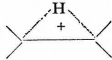
$$E_{\text{corr}} \cong \frac{1}{4} \sum_{p,q} P_{pp} P_{qq} \bar{e}_{pq} \quad (1)$$

were calculated from CNDO/2 wave functions. With open shell systems the half-electron method⁶ was used.

Application Limits of EPCE-F2 σ

Since one-centre $\bar{\epsilon}_{pp}$ are constants and two-centre $\bar{\epsilon}_{pq}$ are functions of interatomic distance, the electronic structure of the molecule is reflected in Eq. (1) only through electron densities over the Slater orbitals of the basis set. Therefore EPCE-F2 σ can give a good account of the correlation energy only in cases where the SCF function itself is a reasonable representation of the exact wave function. Another drawback of EPCE-F2 σ we encountered in our study⁷ was in small clusters of hydrogen atoms. Consider for example a weak complex H₂...H. The SCF wave function dissociates correctly to H₂ + H but the function (1) does not because it predicts a nonvanishing one-centre correlation energy on H in the H₂ + H dissociation limit. Since the hydrogen atom possesses only one electron, its contribution should be zero. Hence, the use of EPCE-F2 σ should be limited to structures with "normal" chemical bonds, unless both the SCF wave function and the function (1) behave correctly in the dissociation limit. In these cases EPCE-F2 σ may be expected to give correlation energies within the ± 0.5 eV error range¹. This tolerance is of course much larger than that required in many chemical problems. In Table I we selected several reactions for which data on the change in correlation energy are available. The entries suggest that generally EPCE-F2 σ cannot be applied to thermochemical problems, which of course is to be expected for such a simple method. However

TABLE I
Correlation Energy Changes (in kJ/mol) in Chemical Reactions

Reaction	EPCE-F2 σ	Reference ΔE_{corr} and type of calculation
2 BH ₃ → B ₂ H ₆	-109.5	- 66.5 CEPA ^a
CH ₃ CH ₂ ⁺ → 	- 21	- 23.5 CEPA ^b
OH ⁻ + H ⁺ → H ₂ O	- 22.2	- 22.2 CEPA ^c
OH [*] + H [*] → H ₂ O	-221.8	-127.9 3rd order perturbation ^d
H ₂ + OH [*] → H ₂ O + H [*]	-122.5	- 39.1 3rd order perturbation ^d
C ₂ H ₂ + 3 H ₂ → 2 CH ₄	-110.4	+ 51.9 "experimental" ^e
N ₂ + 3 H ₂ → 2 NH ₃	- 21.2	- 16.7 "experimental" ^e

^a Ref.⁹; ^b Ref.¹⁰; ^c Ref.¹¹; ^d Ref.¹²; ^e Estimated from SCF energies given by the 6-31G** basis set and experimental heats of reaction¹³.

the first three reactions in Table I indicate that useful results may be obtained for processes where the electronic structures of reactants and products do not differ very much. This is also the case of ionization potentials³. We therefore considered it expedient to explore the application possibilities of EPCE-F2 σ to van der Waals complexes which in our opinion satisfy the requirements noted in this section. Moreover, for the independent electron pair approximation (IEPA), on which EPCE-F2 σ , is based, it was found (*e.g.* ref.⁸) that IEPA intersystem correlation energy matches the dispersion energy for large intersystem distances. In general, EPCE-F2 σ results

TABLE II
Interaction Correlation Energy (in kJ/mol) in van der Waals Complexes

Complex ^a	EPCE-F2 σ	Reference ΔE_{corr}		
		intersystem	total	type of calculation
	- 2.798	-3.578		IEPA ^b
	- 2.605	-1.580		IEPA ^b
	- 0.965	-1.268		IEPA ^b
	-11.385	-4.127		IEPA ^b
	- 4.921	-3.366	0.874	IEPA ^c
	- 7.719		-3.640	CI ^d
	-17.850		-8.159	CI ^d

^a The geometries assumed refer to the van der Waals minima given by the reference calculations; ^b Ref.⁸; ^c Ref.¹⁴; ^d Ref.¹⁵, all single and double excitations from the valence shell are taken into account.

should be closer to IEPA results than to data given by any method in which interactions of electron pairs are accounted for. A typical (though possibly fortuitous) example is provided by the BH_3 dimerization: the correlation energy change given by EPCE-F2 σ is 109.5 kJ/mol, compared to IEPA and CEPA values⁹ of 98.5 and 66.5 kJ/mol, respectively.

van der Waals Complexes

The most abundant data on van der Waals interactions are for noble gases. These however are not amenable to EPCE-F2 σ treatments because the EPCE-F2 σ empirical parameters were derived for H, B, C, N, O and F atoms. We selected therefore complexes which contain only the noted atoms and for which reliable nonempirical calculations were reported. The $\text{H}_2 \cdots \text{H}_2$ complex was disregarded in this paper because it has been treated by us previously⁷. We also disregarded all complexes containing the F_2 molecule because EPCE-F2 σ does not work well¹ for F_2 . (We found that interaction correlation energies in these complexes are drastically overestimated.) The complexes assumed are summarized in Table II.

Let us start the discussion of entries in Table II with the HF dimer because the data for this complex are the most complete. It is seen that the EPCE-F2 σ data match the IEPA intersystem rather than the total interaction correlation energies. From the data on the other complexes it appears that there is a general trend between the EPCE-F2 σ total and IEPA intersystem energies. Hence a question may be asked whether either the intrasystem correlation energy is not accounted for by EPCE-F2 σ or the intersystem correlation energy is overestimated. We favour the second view. As seen from Eq. (1), the change in the intrasystem correlation energy upon complex formation is given, within the frame of EPCE-F2 σ , only through electron densities. Since CNDO/2 gives reasonable charge distributions, the intrasystem correlation energy should be accounted for in some way by EPCE-F2 σ . We tested this assumption numerically. Upon bringing two HF molecules from infinity to the intersystem distance corresponding to the van der Waals energy minimum, we obtained for the EPCE-F2 σ intrasystem correlation energy the change of +3.474 kJ/mol, in very good agreement with the IEPA value of +4.240 kJ/mol. From this it follows that, compared to IEPA, EPCE-F2 σ overestimates the intersystem component of the interaction correlation energy.

Besides the CI calculations noted in Table II, there is available also for the water dimer a very accurate calculation¹⁶ on the dispersion energy. This calculation predicts for the van der Waals minimum the dispersion energy of 6.443 kJ/mol. The authors¹⁶ mean that this value is 20% lower than the actual dispersion energy. Our EPCE-F2 σ prediction is in remarkable agreement with their estimate. We wish to present also data for the ethylene dimer with the sandwich structure. In this case the *ab initio* valence-bond calculations by Wormer and van der Avoird¹⁷ gave no van der Waals

minimum and the system was therefore not included in Table II. For $R = 0.32$ nm Mulder and coworkers¹⁸ arrived at the dispersion energy of 5.11 kJ/mol, compared to the EPCE-F2 σ value of 16.79 kJ/mol. At 0.265 nm the dispersion energy was 48.15 kJ/mol¹⁸, compared to the EPCE-F2 σ value of 28.95 kJ/mol.

To conclude, we summarize briefly our experience acquired with EPCE-F2 σ . Though the overall agreement with nonempirical calculations is reasonable, the EPCE-F2 σ results should not be overestimated. As any semiempirical MO method, EPCE-F2 σ is more suited for qualitative estimates of trends rather than quantitative predictions. In the region of the van der Waals minimum, EPCE-F2 σ mimics the IEPA intersystem interaction correlation energy. At shorter distances, the EPCE-F2 σ interaction energies are too high and at larger distances they are too low and cannot therefore be employed for the determination of the C_6 , C_8 , C_{10} ... coefficients of the asymptotic expansion of the dispersion energy. The reported data for the $H_2 \cdots HF$ and $H_2 \cdots H_2O$ complexes made it possible to treat these complexes in two conformations. We consider it important that EPCE-F2 σ reproduces correctly the order of stabilities. EPCE-F2 σ might also be very useful for treatments of large clusters for which more sophisticated calculations are not feasible. If for a pair of particular systems the interaction energy is well accounted for by EPCE-F2 σ , it may be anticipated that larger clusters of these systems will be amenable to treatments by EPCE-F2 σ .

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