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Semiempirical Estimates of the Correlation Energy in Small Clusters of Hydrogen Atoms

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The Pamuk EPCE-F2σ method is applied to neutral and charged clusters composed from 2–9 hydrogen atoms. The range of applicability of the method is demonstrated with H_2, H_3^+, and H_3 by comparing the results with the reported rigorous SCF and CI calculations. Predictions of the correlation energy were made for larger hydrogen atom systems, the emphasis being laid in the discussion on H_4, H_5^+, and H_6.

Key words: Hydrogen atom clusters, correlation energy of ~

1. Introduction

Since the near Hartree-Fock calculations become now feasible for larger than triatomic molecules, the correlation energy represents one among the most serious bottlenecks in the quantum chemical approaches to chemical reactivity. Although much progress has been made in the electron pair theories [1] and configuration interaction techniques [2], the actual calculations beyond the Hartree-Fock limit are, compared to SCF calculations, still rather complex and time consuming. It is therefore expedient to look for simpler semiempirical ways of calculation [3–6], in spite of the anticipated lower accuracy and reliability. In this paper we treat the EPCE-F2σ method of Pamuk [4]. The method is expected [5] to give correlation energies within the ±0.5 eV error range. Although this tolerance is much larger than that required in many chemical problems, the feasibility of the calculations warrants attempts for the applications. The aim of this paper is to show the virtues and the limitations of the method with the hydrogen-atom systems. The method is first tested against the *ab initio* data for H_2, H_3^+ and H_3. Next it is applied to larger hydrogen-atom clusters. The H_2–H_2 complex is treated separately because of its primary importance.

2. Calculations

We follow closely the Pamuk EPCE-F2σ method [4], which for hydrogen-atom systems gives the correlation energy in the following form

$$E_{\text{corr}} \cong \frac{1}{4} \sum_{p,q} P_{pp} P_{qq} \bar{\varepsilon}_{pq} \tag{1}$$

The electron densities,

$$P_{pp} = \sum_{k} n_k c_{kp} c_{kp} \tag{2}$$

were evaluated by standard CNDO/2 calculations; with open shell systems the SCF procedure of Longuet-Higgins and Pople [7] was used. The orbital occupancies are $n_k = 2$ for doubly occupied orbitals and $n_k = 1$ for singly occupied orbitals. The one-center effective pair correlation energy, $\bar{\varepsilon}_{1s^2}$, was fixed [8] at -1.08 eV.

3. A Remark on the Use of the EPCE-F2σ Method

The ideal way of how to exploit adequately any approximate method is to test it against a rigorous method and then, with the knowledge of its feeble points, to apply it to systems where the rigorous calculations are not manageable. In our case the first of the two steps is rather difficult, because reliable correlation energies are available only for H_2, H_3^+ and H_3. Nevertheless even a treatment of this limited series of systems gives us useful results. These are shown in Figs. 1–3. The rigorous correlation energy is taken here to be the difference between the energies given by the near Hartree-Fock and the near complete CI calculations (with H_2 by exact non-relativistic [9] and exact Hartree-Fock [10] calculations). For H_3^+ we made use of the data of Carney and Porter [11] for the equilateral geometries. From the potential energy surface reported by Liu [12] for H_3 we selected several points lying close to the reaction path of the $H + H_2 \rightarrow H_3$ process. Figs. 1 and 2 show that

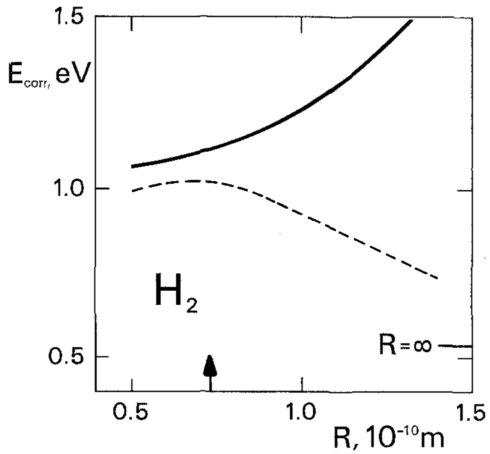

Fig. 1. Dependence of the correlation energy in H_2 on the interatomic distance. Full line – *ab initio* [9, 10], dashed line – EPCE-F2σ. The arrow at the left bottom indicates the equilibrium H–H distance [10]

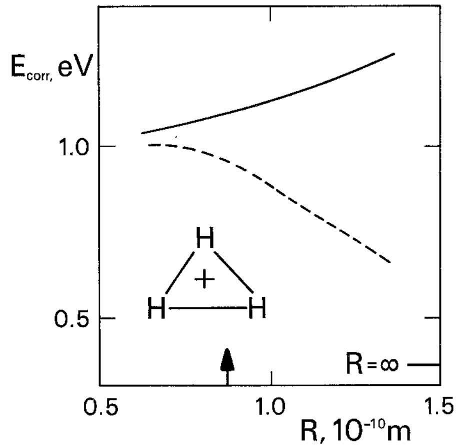

Fig. 2. Dependence of the correlation energy in the equilateral H_3^+ on the symmetric molecular stretch. Full line – *ab initio* [11], dashed line – EPCE-F2σ. The arrow at the bottom indicates the equilibrium geometry [11]

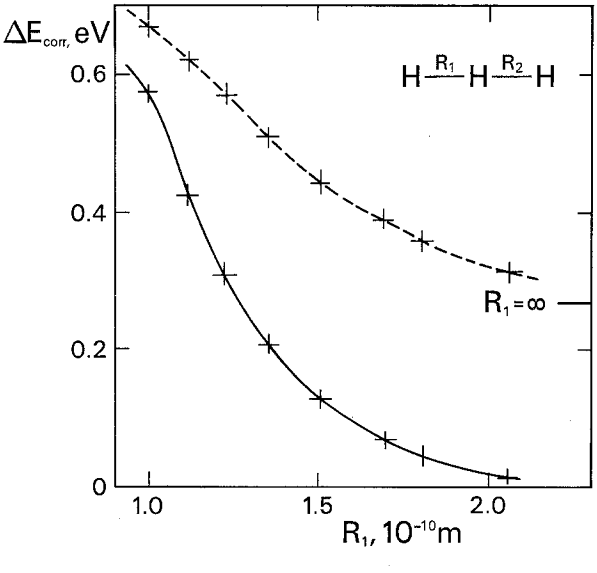

Fig. 3. Dependence of the correlation energy change in the $H_3 \rightarrow H_2 + H$ process. ΔE_{corr} is the difference in correlation energy between H_3 and $H_2 + H$. The points marked represent roughly the reaction path [12] and refer to $R_2 = 0.89$, 0.84, 0.81, 0.80, 0.78, 0.77, 0.77 and 0.76×10^{-10} m. Full line – *ab initio* [12], dashed line – EPCE-F2σ

the EPCE-F2σ method gives a good account of the correlation energy for the portion of the energy surface near the equilibrium geometry. The failure in the region more remote from the equilibrium geometry is due to the fact that EPCE-F2σ is applicable only in cases where the SCF function is a reasonable representation of the exact wave function. The increasing discrepancy between the semi-empirical and exact correlation energies in H_3 along the reaction path (Fig. 3) is due to an inherent shortcoming of the EPCE-F2σ method. Though the SCF wave function dissociates correctly to H_2+H, the functional (1) does not – it predicts a nonvanishing one-center correlation energy on H in the H_2+H dissociation limit (since the hydrogen atom possesses only one electron, its contribution should be zero). The same artifact of the "residual" correlation energy is also met in the dissociation limit of H_2 (cf. Fig. 1). To summarize, the use of the EPCE-F2σ method should be limited to structures with "normal" chemical bonds, unless both the SCF wave function and the functional (1) behave correctly in the dissociation limit.

4. Applications to Clusters of Hydrogen Atoms

For H_3^- the correlation energy is available [13] for the symmetrical linear structure with $R=1.169\times10^{-10}$ m. The EPCE-F2σ method reproduces it (Table 1) with the error not exceeding the ±0.5 eV range. For H_4^{2+} we employ two geometries given by the *ab initio* calculations [14]: a square with $R=1.191\times10^{-10}$ m and a tetrahedron with $R=1.259\times10^{-10}$ m. Our calculations predict that the correlation energy in the latter is 0.046 eV higher. H_4^+ was disregarded in our considerations because of its structure. According to *ab initio* calculations [15] H_4^+ is a weak complex between H_3^+ and H with the separation as large as 2.6×10^{-10} m. Obviously, EPCE-F2σ would overestimate its correlation energy, giving an unrealistic one-center contribution on the hydrogen atom. H_5^+ belongs to the family of odd H_n^+ ions observed mass-spectrometrically. The geometry of the ion is

Table 1. Correlation energies in hydrogen-atom systems

System	Geometry[a, b]	Correlation energy[c]	
		EPCE-F2σ	*ab initio*[b]
H_2	$R=0.741$	1.008	1.113
H_3^+	equilateral triangle, $R=0.873$	0.943	1.092
H_3	linear, $R_1=R_2=0.926$	1.703	1.724
	linear, $R_1=R_2=0.741$	1.883	
H_3^-	linear, $R_1=R_2=1.169$	2.416	1.997
H_4^{++}	square, $R=1.191$	0.627	
	tetrahedron, $R=1.259$	0.673	
H_5^+	C_{2v}, fully optimized	2.165	
	C_{2v}, H_3^+ equilateral, $R=1.532$	2.188	
H_5	linear equidistant, $R=0.741$	3.722	
H_5^-	pentagon, $R=1.041$	3.775	
H_6	equilateral triangle, $R=1.588$	4.432	$3C-0.053$[d]
	linear equidistant, $R=1.588$	3.968	$3C+0.006$[d]
H_7^+	equilateral H_3^+, $R=1.532$	3.448	
H_9^+	equilateral H_3^+, $R=2.532$	4.729	

[a] See Fig. 4, interatomic distances in 10^{-10} m.

[b] For references see text.

[c] In eV.

[d] Only relative values are available, C is the correlation energy in H_2.

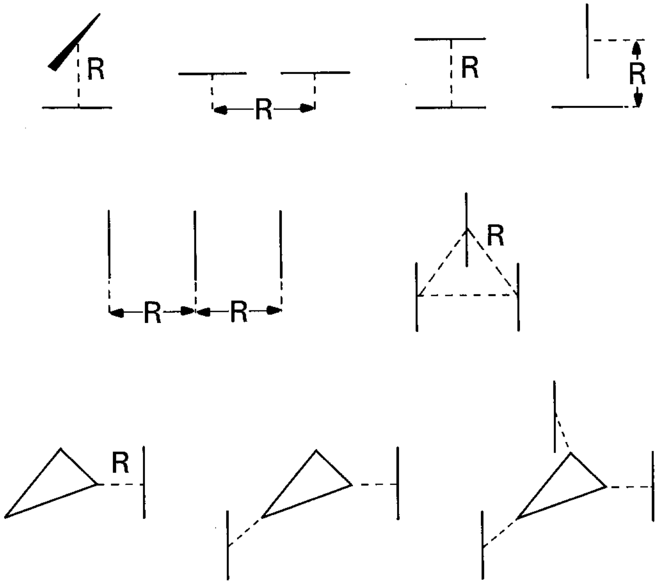

Fig. 4. Assumed geometries for H_4, H_6, H_5^+, H_7^+ and H_9^+. *R* are specified in Tables

predicted by *ab initio* calculations [16] to correspond to an $H_3^+ \ldots H_2$ complex of C_{2v} symmetry (Fig. 4). The correlation energy was computed for the optimized geometry [17] given by the [2*s*1*p*] basis set. For the sake of comparison with H_7^+ and H_9^+ ions we made also use of another geometry: H_3^+ is assumed in its optimal equilateral geometry but the H–H distance in H_2 and *R* (cf. Fig. 4) are taken from the optimal H_5^+ geometry [17]. H_7^+ and H_9^+ were then constructed in a similar way, placing one and two H_2 molecules to the remaining H_3^+ apexes with the same *R* (cf. Fig. 4). Correlation energy of H_5^+ plays an important role in the estimation of the binding energy of the complex. Since both H_3^+ and H_2 are closed shell species and the interaction is weak, the change of the correlation energy in the $H_3^+ + H_2 \rightleftharpoons H_5^+$ reaction should be small, perhaps comparable to the van der Waals attraction in $(H_2)_2$. To judge the value given by the EPCE-F2σ method, we attempted to estimate the correlation energy in H_5^+ by means of the calculation of the dispersion energy for the T shaped $(H_2)_2$ dimer. The assumed intermolecular separation was the same as in H_5^+ – the distance between centers of the two H_2 molecules was taken as the sum of the equilibrium *R* in H_5^+ and the half H–H distance in H_2. By making use of the relationship of Victor and Dalgarno [18] we arrived at the dispersion energy[1] of 15.5 kJ/mol. This is in reasonable agreement with the correlation energy change in the $H_3^+ + H_2 \rightarrow H_5^+$ reaction given by EPCE-F2σ (21 kJ/mol, cf. Table 1). Nevertheless we think that the correlation energy given by EPCE-F2σ for H_5^+ is overestimated. This can be anticipated on the basis of results for $(H_2)_2$, since the intermolecular distance in the H_5^+ complex falls into

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[1] For the sake of convenience we express hereafter the dispersion energies in kJ/mol (1eV = 96.487 kJ/mol).

the range where EPCE-F2σ overestimates the correlation energy in the T shaped $(H_2)_2$ (*vide infra*). With H_5 and H_5^- there is no evidence for the potential minima. Our estimates of correlation energies are made for the idealized equidistant linear structure of H_5 and the optimal pentagon structure of H_5^- given by CNDO/2. H_6 in a hexagonal structure has been previously calculated by Sinanoğlu and Pamuk [8]. We carried out the calculation for two other geometries that were assumed by Ree and Bender [19] in their *ab initio* study. These represent clusters of three H_2 molecules ($R_{HH}=0.741\times10^{-10}$ m) in equilateral and linear structures (cf. Fig. 4). Though with H_6 the EPCE-F2σ method should be free of the shortcomings outlined in the preceding section, the results given by the EPCE-F2σ and *ab initio* calculations are contradictory. The former predicts 0.464 eV more correlation energy in the triangular structure than in the linear structure, the latter favours the linear structure by 0.059 eV. As will be shown with the $(H_2)_2$ dimer, EPCE-F2σ overestimates the correlation energy at lower intermolecular distances. In the triangular $(H_2)_3$ there are three short-range interactions, whereas in the linear structure there are two. This is a probable reason why the Pamuk method predicts the incorrect order of correlation energies in the two configurations. This suggests that the EPCE-F2σ results should be taken with caution in conformational problems if the distance between the two nearest neighbouring nonbonded H atoms is shorter than about 2.7×10^{-10} m. On the other hand, long-range interactions in van der Waals molecules seem to be amenable to treatments by EPCE-F2σ.

5. The H_2–H_2 Complex

The H_2–H_2 complex is of particular importance among the systems studied because it may be exploited to show the way of how to arrive at the interaction energies between larger systems. We consider four $(H_2)_2$ structures shown in Fig. 4. The correlation energies given by the Pamuk method are compared in Table 2 with the data reported on correlation energies resulting from *ab initio* calculations and on dispersion energies. Among the data available [18, 20–24] we selected the results of Kochanski and collaborators [22] because their SCF-CI calculation was performed with a sufficiently large basis set involving polarization functions so chosen as to give a good account of the dispersion energy. The dispersion energies [23, 24] are presented in Table 2, too, because they can be identified with the intermolecular correlation energies at larger distances. We now comment on the stability of configurations due to the correlation (dispersion) energy. The EPCE-F2σ method gives the order linear, T shaped, rectangular, D_{2d}. The same order results from the dispersion energies. With the correlation energies reported by Kochanski and coworkers [22] the order of the two last configurations is interchanged. The energy differences between the configurations are markedly larger with the EPCE-F2σ data than they are with the other procedures. If the distance between nearest neighbouring nonbonded H atoms is larger than about 2.7×10^{-10} m, EPCE-F2σ data agree well with the others, at shorter distances they are overestimated. To summarize, EPCE-F2σ predicts correctly the order of stabilities of the $(H_2)_2$ configurations, but overestimates the correlation energies

Table 2. Intermolecular correlation and dispersion energies in the $(H_2)_2$ complex

$R^{a,b}$	Correlation energy^{c,d}		Dispersion energy^{c}	
	EPCE-F2σ	Ref. [25]	Ref. [24]	Ref. [18]
D_{2d} configuration^{b}				
2.6459	−2.6393	−1.8509	−1.2174	−1.8706
2.9105	−1.1686	−1.3022	−0.7141	−1.0560
3.1751	−0.5021	−0.9557	−0.4303	−0.6264
3.4397	−0.2100	−0.7167	−0.2670	−0.3875
3.7043	−0.0862	−0.5225	−0.1709	−0.2484
3.9689	−0.0343	−0.3702	−0.1124	−0.1641
Linear configuration^{b}				
2.6459	−7.8613	−2.8355	−2.9870	−2.5672
2.9105	−3.8003	−1.9061	−1.7110	−1.4490
3.1751	−1.7556	−1.2865	−0.9995	−0.8598
3.4397	−0.7812	−0.8506	−0.5960	−0.5319
3.7043	−0.3368	−0.5566	−0.3657	−0.3408
3.9689	−0.1414	−0.3597	−0.2313	−0.2253
Planar rectangular configuration^{b}				
2.6459	−2.6740	−1.8221	−1.3392	−1.9042
2.9105	−1.1824	−1.2602	−0.7774	−1.0749
3.1751	−0.5071	−0.9032	−0.4642	−0.6377
3.4397	−0.2121	−0.6642	−0.2859	−0.3943
3.7043	−0.0866	−0.4805	−0.1817	−0.2528
3.9689	−0.0347	−0.3413	−0.1192	−0.1672
T shaped configuration^{b}				
2.6459	−4.6706	−2.1213	−1.8767	−2.1516
2.9105	−2.1510	−1.4755	−1.0833	−1.2145
3.1751	−0.9427	−1.0266	−0.6401	−0.7204
3.4397	−0.3992	−0.7220	−0.3888	−0.4458
3.7043	−0.1724	−0.5303	−0.2434	−0.2856
3.6989	−0.0707	−0.3833	−0.1570	−0.1887

[a] Intersystem separation in 10^{-10} m.
[b] See Fig. 4.
[c] In kJ/mol.
[d] The entries are respective differences in correlation energies of $(H_2)_2$ and $2H_2$.

in absolute value at shorter distances. The overestimation becomes significant in configurations with a close approach of two atoms (with $(H_2)_2$ in the linear configuration). Finally, we note on the total interaction energies in $(H_2)_2$. We treat here the total interaction energy as the sum of the SCF energy and the correlation energy given by EPCE-F2σ. The SCF interaction energies were calculated with the [2*s*] basis set by making use of the Boys-Bernardi function counterpoise method [26]. Previously we have demonstrated [27, 28] that this procedure gives results comparable to those given by the [4*s*2*p*] basis set. The total interaction energies (Table 3) predict energy minima for the linear and T shaped configurations. The minimum in the former is overestimated which is due to the overestimation of the correlation energy in this configuration. Compared to results of Ref. [22], the total interaction energy is of comparable value with the T shaped configuration, over-

Table 3. Interaction energies[a] in the $(H_2)_2$ complex

$R^{b,c}$	SCF	Correlation (EPCE-F2σ)	Total	SCF	Correlation (EPCE-F2σ)	Total
	D_{2d} configuration[c]			Linear configuration[c]		
2.6459		−2.6393			−7.8613	
2.9105	1.8087	−1.1686	0.6401	2.9585	−3.8003	−0.8418
3.1751	0.7397	−0.5021	0.2376	1.2857	−1.7556	−0.4699
3.4397	0.3029	−0.2100	0.0929	0.5669	−0.7812	−0.2143
3.7043	0.1243	−0.0862	0.0381	0.2623	−0.3368	−0.0745
3.9689	0.0523	−0.0343	0.0180	0.1322	−0.1414	−0.0092
	Planar rectangular configuration[c]			T shaped configuration[c]		
2.6459	4.5375	−2.6740	1.8636	5.0961	−4.6706	0.4255
2.9105	1.8891	−1.1824	0.7067	2.082	−2.1510	−0.0690
3.1751	0.7904	−0.5071	0.2833	0.8167	−0.9427	−0.1260
3.4397	0.3356	−0.2121	0.1234	0.3071	−0.3992	−0.0921
3.7043	0.1469	−0.0866	0.0602	0.1075	−0.1724	−0.0649
3.9689	0.0682	−0.0347	0.1381	0.0318	−0.0707	−0.0389

[a] By interaction energies we imply the respective energy differences between $(H_2)_2$ and $2H_2$, all energies are in kJ/mol.

[b] Intersystem separations in 10^{-10} m.

[c] See Fig. 4.

estimated with the linear configuration and underestimated with the planar rectangular and D_{2d} configurations. Qualitatively, however, the predictions are correct.

6. Conclusions

The results on the hydrogen-atom systems conform to the claim [5] that EPCE-F2σ gives correlation energies within the ±0.5 eV error range. The method is inherently incapable to give a good account of correlation energies for structures with "long" chemical bonds if the SCF wave function and/or the functional (1) do not behave correctly in the dissociation limit. The method overestimates the correlation energy in weak complexes of closed shell molecules with the approach of two H atoms closer than about 2.7×10^{-10} m. The results for $(H_2)_2$ suggest, however, that the correlation energy is well accounted for in van der Waals molecules at longer intermolecular distances. This implies that EPCE-F2σ might be useful in applications to larger van der Waals complexes. In spite of a computational progress in CI treatments, the direct calculations of the interaction energy are still feasible only with small systems. The drawback in the perturbation calculations of the dispersion energy is that one can arrive at reasonable values only by augmenting the AO basis set for polarization functions with the optimized exponents[2]. The EPCE-F2σ method gives us here a chance that the interaction energies could be computed at considerably lower cost. If the total interaction energy is assumed as the sum of the SCF interaction energy and the correlation energy, the former can be calculated reasonably with a small basis set by making

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[2] In contrast to SCF energies, optimal dispersion energies are obtained for low values of exponents.

use of the idea of the Boys-Bernardi method and the latter can be estimated by EPCE-F2σ. In the present paper we applied this procedure to $(H_2)_2$..In the future we hope to be able to apply it to some larger systems.

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