

## A CEPA2 Study of the H<sub>2</sub>-H<sub>2</sub> Isotropic Potential Function

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### Abstract

A CEPA2 study of the DD<sup>1</sup> (Koide and Kihara 1974) conformation of two hydrogen molecules has been carried out using a basis set consisting of 102 independent gaussian functions to describe the interacting system. Calculations using a smaller basis set indicate that this conformation provides a close approximation to the isotropic  $V_{000}$  potential function. The study was carried out for intermolecular separations ranging from  $R=2.0$  to  $15.0$  a.u. keeping the H<sub>2</sub> bondlengths fixed at  $r=1.449$  a.u. The well depth was determined to be  $104.73$   $\mu$ h at  $R_m=6.597$  a.u. and the zero point crossing at  $R_0=5.825$  a.u.

### 1. Introduction

In order to feasibly obtain realistic descriptions of the potential functions between atoms and/or molecules by *ab initio* techniques, approximations which will minimise deviation from the exact result need to be invoked. Such approximations involve compromises in both the completeness of the basis set and the computational formalism used to describe the detailed electronic structure of the interacting system.

If one of the interacting species in such calculations is a molecule, two further approximations are generally adopted to describe the interaction. Firstly, the rigid rotor approximation is invoked, where the bond lengths of the interacting species are kept constant over the entire range of the interaction. Secondly, a finite number of angular conformations are used to determine the isotropic and anisotropic terms of the interaction.

In the present study a large basis set capable of giving an accurate description of the energetically important terms in the interaction is used in conjunction with a computational formalism which will provide most of the electron correlation energy for this interaction. The resulting data should thus provide an accurate description of the self-consistent field (SCF) energy change and the intra- and inter-correlation energy changes over the potential function. The rigid rotor approximation, which has been shown to have a very minor influence on a potential function similar to the present study (Senff and Burton 1985), has also been used.

Since both a near-complete basis set and computational formalism were used to describe the interaction, a further approximation needed to be made to make the present study computationally feasible. This approximation involved finding only one conformation of the interacting species which would describe the isotropic interaction. Studies using a smaller basis set suggest that the selected conformation fulfils this criterion.

The 15 internuclear distances sampled in the present study represent approximately 2500 hours of dedicated Sperry 1100/72 computer time at the University of Wollongong. Typical calculations involved interim data storage volumes of about 350 megabytes.

Although a full configuration interaction (CI) calibration of the coupled electron pair approximation (CEPA2) method was considered with the present basis, this was not feasible. A full CI calibration of the CEPA2 method when applied to a calculation of the  $\text{He}_2$  interaction with a similar sized basis (Senff and Burton 1986) was not feasible at the time on one of the world's latest supercomputers (P. R. Taylor, personal communication).

## 2. Method

The present work involves calculating the SCF energy of the interacting system, or supermolecule. The electron correlation energy is then taken into account using the CEPA2 method, developed by Meyer (1971, 1973) and somewhat independently by Ahlrichs *et al.* (1975*a*, 1975*b*). This involves determination of pair natural orbitals (PNOs) from the Hartree-Fock molecular orbitals within the independent electron pair approximation (IEPA). The PNOs obtained within this framework can then be used to determine the pair natural orbital configuration interaction (PNOCI) correlation energy or the more reliable CEPA2 approximation to the electron correlation energy. The procedure used in determining the various correlation energies has been described by Ahlrichs *et al.* (1975), who provided the original computer code which was developed to generate the present results.

Separation of the electron correlation energy into intra- and inter-system correlation terms was based on localised occupied orbitals derived from SCF molecular orbitals via Boys' (1960) criterion.

The intra-correlation energy results from allowing double substitutions within the orbitals of each subsystem. It accounts for most of the total correlation energy, but when energy differences are taken to describe a potential function it makes a small but significant contribution. This contribution is mainly due to the exclusion effect caused by the other interacting subsystem, which diminishes the total intra-correlation energy.

The inter-correlation energy results from double substitutions between orbitals of the two interacting subsystems. This energy term is similar to the dispersion term obtained from perturbation theory calculations.

The two correlation energy terms cannot be successfully determined separately because the coupling terms between them have a significant effect in modifying the uncoupled energies (Maeder and Kutzelnigg 1976). Since the two correlation energy terms require different basis functions for their optimum representation, the energies and their coupling terms can only be properly accounted for by using the one large basis set to describe them.

The performance of the CEPA2 method in representing the electron correlation energy was initially determined by Meyer (1971, 1973) and Ahlrichs *et al.* (1975*a*, 1975*b*). A comparison with the more complete coupled pair approximation has been carried out by Taylor *et al.* (1976, 1978*a*, 1978*b*, 1979). A more relevant evaluation of the CEPA2 procedure to the present work has been carried out by Harrison and Handy (1983) and Burton (1983). In these studies the CEPA2 correlation energy was compared with that obtained from a full CI calculation. The studies showed that, when a large basis set was used to represent the interaction energy of two hydrogen molecules in the T conformation near their van der Waals minimum, the CEPA2 procedure underestimated the well depth by about 3%. This underestimation of the potential well is primarily due to the neglect of triple excitations in the CEPA2 method. Thus, the present results will contain a small error in regions of the potential dominated by the attractive (inter-correlation) component of the interaction primarily for this reason. However, because of the basis set size used in the present calculation, these errors will be significantly smaller than those from any other calculation which has attempted to describe the potential function for this system.

Determination of which conformation (if any) of two hydrogen molecules would closely approximate the isotropic terms for all  $R$  was made using the basis set and data of two previous studies (Burton and Senff 1982, 1983) supplemented by some additional calculations. Since most of the data of those studies was obtained using IEPA to obtain the correlation energy, initial comparisons were made at this level of computation, even though IEPA *systematically* overestimates correlation energies (i.e. there is a near linear relationship between IEPA and CEPA2 intercorrelation energies for the weakly coupled pairs of this work).

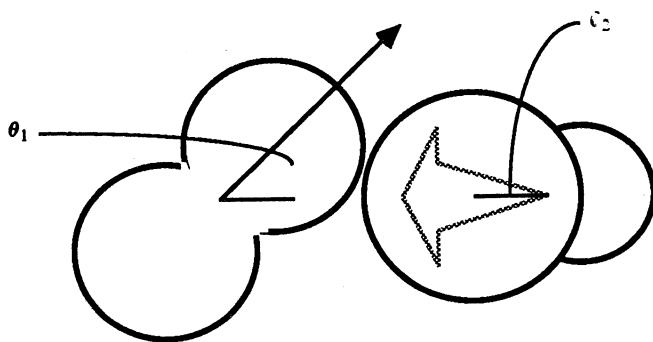


Fig. 1. The DD' configuration with  $\theta_1 = \theta_2 = 60^\circ$ .

As a reference point, the  $V_{000}$  energies obtained from a weighted average of the generally used linear, parallel, T and crossed conformations at three intermolecular separations were used. For  $R = 4.0, 6.5$  and  $9.0$  a.u. ( $1 \text{ a.u.} \equiv 52.9177 \text{ pm}$ ), the IEPA energies were  $7251.09, -149.80$  and  $-32.75 \mu\text{h}$  ( $1 \text{ h} \equiv 3.808 \times 10^{-4} \text{ kJ mol}^{-1}$ ). The respective energies for the DD<sup>1</sup> conformation (shown in Fig. 1) were  $7053.36, -149.30$  and  $-32.15 \mu\text{h}$ . When nine conformations rather than four were used to determine the  $V_{000}$  term at

$R = 6.5$  a.u. the IEPA energy was  $-145.78 \mu\text{h}$ . Using the CEPA2 method to obtain the correlation energy at  $R = 6.5$  a.u. gives results of  $-80.11$  and  $-76.90 \mu\text{h}$  for the four and nine term approximations to  $V_{000}$  respectively, while the result for the  $\text{DD}^1$  calculation was  $-82.54 \mu\text{h}$ .

Although deviation of the  $\text{DD}^1$  result from the  $V_{000}$  term is increased when a weighted average of nine conformations is used to approximate this term instead of four conformations, it is not presently known if improved approximations to the  $V_{000}$  term would continue to deviate from the  $\text{DD}^1$  energy or again move towards it. Therefore, since agreement with the standardly used four term approximation was considered satisfactory, improved calculations using this interaction symmetry for  $\text{H}_2\text{-H}_2$  were carried out with a larger basis set, as given in Table 1.

**Table 1. Gaussian basis used**

Nucleus	Midbond
6s(2, 1, 1, 1, 1) <sup>A</sup>	1f(0.2)
4p(0.03, 0.12, 0.5, 2.0)	
1d(0.3)	

<sup>A</sup> Basis functions of Huzinaga (1965).

This basis set is similar to the hydrogen basis set used in a study of the He- $\text{H}_2$  interaction (Senff and Burton 1985). Differences in the bases are that, in the present study, the s, p bond functions were omitted to make the computations computationally feasible, and the midbond f exponent was increased from 0.08 to 0.20 in order to improve the description of the potential well region of the interaction. In all, 102 independent functions (51 per  $\text{H}_2$ ) were included in the atomic orbital basis set. Compared with the initial studies of this interaction (78 functions in total) (Burton and Senff 1982, 1983) the most important changes involved the replacement of the midbond functions by similar nuclear centred d functions and the addition of f functions to midbond.

It is expected that this basis set should give a reliable description of the various energy terms contributing to the total interaction. It is composed of both diffuse functions necessary to describe the inter-correlation energy and more compact functions which are necessary to describe the SCF and intra-correlation energy in the short range interaction.

Since both the present basis set and computational formalism are capable of giving a good description of the  $\text{H}_2\text{-H}_2$  interaction, the major cause of any deviation from a definitive representation of the  $V_{000}$  interaction will probably be from the approximation of using only one representative geometry for this term. The conjunction of the fixed ( $r_0$ ) rigid rotor geometry for each  $\text{H}_2$  and the choice of  $\text{DD}^1$  as representative of the  $V_{000}$  angular average (which otherwise necessitates four, six, nine or more independent geometries being considered) at each internuclear distance combine to make the present study feasible. A full geometry investigation comparable with the previous He- $\text{H}_2$  study (Senff and Burton 1985) would involve a commitment of 45,000 hours of Sperry 1100/72 time.

### 3. Results and Discussion

SCF, IEPA, CEPA2 and PNOCI energy changes over the potential function are presented in Table 2. All data have been corrected for the effects of basis set superposition error (BSSE) using the function counterpoise method of Boys and Bernardi (1970), as included in Table 2. Considering the completeness of the basis set used, the corrections to the SCF energy show that the basis set is virtually complete for this level of study. When correlation energy is included in the computations, the BSSE corrections are significantly larger and amount to about 20% of the determined well depth. Although this correction can still be considered large, it is significantly smaller than ever achieved before on a van der Waals interaction when large basis sets have been used. Since the correction depends on the degree that one subsystem can utilise the functions of the other, a smaller BSSE correction could be achieved with a smaller, more compact basis set. However, this would be at the expense of correctly modelling the various energy terms. The size of the corrections at the correlation level of computation also suggests that a basis set would need to be significantly larger than the present before corrections at the correlation level of computation were of similar size to the present SCF corrections. Basis sets of the required size to achieve such a result currently present intractable computational problems for a study even as simple as the interaction of two hydrogen molecules.

**Table 2. Interaction energies and BSSE corrections ( $\mu\text{h}$ )**

The CEPA2 BSSE correction is the total correction and includes the SCF BSSE correction

R (a.u.)	$\Delta E$					BSSE corrections	
	SCF	IEPA	CEPA2	PNOCI		SCF	CEPA2
2.0	204739.31	191012.83	193947.91	194724.00		13.59	516.17
3.0	49015.22	41457.20	42948.95	43376.87		3.56	222.33
4.0	10137.18	6946.60	7574.59	7759.06		2.74	110.09
5.0	1868.91	637.07	890.95	965.73		1.80	57.20
5.5	773.09	14.41	176.26	223.63		1.25	41.78
6.0	311.94	-158.58	-54.57	-24.46		0.80	28.21
6.5	122.35	-171.76	-104.15	-84.83		0.69	20.21
7.0	46.17	-141.81	-97.23	-84.67		0.64	13.72
8.0	4.98	-75.29	-54.89	-49.32		0.43	7.62
9.0	-0.42	-38.23	-28.21	-25.56		0.31	4.04
10.0	-0.71	-19.99	-14.72	-13.36		0.24	2.34
11.0	-0.48	-11.05	-8.11	-7.33		0.15	1.62
12.0	-0.28		-4.61	-4.16		0.10	1.15
13.0	-0.15	-3.88	-2.82	-2.54		0.05	0.81
15.0	-0.02	-1.58	-1.14	-1.01		0.01	0.39

Comparing the present SCF energies for the DD<sup>1</sup> conformation with those obtained with the 78 function basis (Burton and Senff 1982, 1983) at  $R=4.0$ , 6.5 and 9.0 a.u. gives 10137.18, 122.35 and -0.42  $\mu\text{h}$  for the present basis and 10155.17, 123.09 and -0.43  $\mu\text{h}$  for the 78 function basis. Slightly less repulsive values are obtained in the present study due to the improved flexibility the larger basis gives in describing the molecular orbitals.

When the CEPA2 electron correlation energy is included in the calculations, the improvement in going from the 78 function basis to the present is more pronounced. The CEPA2 energies at  $R=4.0$ ,  $6.5$  and  $9.0$  a.u. are  $7574.59$ ,  $-104.15$  and  $-28.21 \mu\text{h}$  respectively for the present basis and  $7678.93$ ,  $-82.54$  and  $-23.67 \mu\text{h}$  for the smaller basis. The present basis gives an improved description of the  $\text{H}_2$  multipole moments and polarisability components [this is inferred due to the close connection between the present basis and basis  $A^1$  for  $\text{H}_2$  in Burton and Senff (1982)] compared with the 78 function basis, thus improving the description of the inter-correlation energy term significantly.

In the present study the CEPA2 minimum occurs at  $R_m = 6.597$  a.u. with a well depth  $\epsilon$  of  $-104.73 \mu\text{h}$  and a zero point crossing at  $R_0 = 5.825$  a.u.

Differences between the PNOCI and CEPA2 energies give the contribution of the coupled pairs (quadruple excitations) to the interaction. At  $R=6.5$  a.u. this amounts to about 19% of the CEPA2 well depth. Comparison of the CEPA2 and IEPA energies shows how the strength of the interaction is overestimated when omitting the effects of inter-intra coupling as well as decoupling the inter singlet and triplet pairs. At  $R=6.5$  a.u., the IEPA well depth overshoots the CEPA2 well by about 65%. PNOCI (no simultaneous double excitations) is variational but systematically underestimates interaction correlation energies.

**Table 3. Intra-correlation energies ( $\mu\text{h}$ )**

Here and in Table 4  $c$  stands for correlation energy including the effects of intra-inter coupling, while  $u$  represents the uncoupled correlation energy

$R$ (a.u.)	IEPA	CEPA2 $c$	CEPA2 $u$	PNOCI $c$	PNOCI $u$
2.0	6723.57	7185.26	7022.18	7419.85	6698.64
3.0	1228.07	1580.55	1263.45	1732.45	1178.64
4.0	227.49	404.04	231.67	469.00	207.89
5.0	43.76	120.85	44.20	146.56	38.29
5.5	19.33	69.53	19.46	85.64	16.82
6.0	7.69	40.40	7.73	50.55	6.68
6.5	3.84	25.28	3.85	31.76	3.54
7.0	1.02	15.23	1.03	19.43	1.04
8.0	0.84	7.34	0.84	9.21	0.98
9.0	0.29	3.48	0.29	4.36	0.39
10.0	0.19	1.93	0.19	2.31	0.25
11.0	0.18	1.11	0.18	1.37	0.23
12.0	0.11	0.65	0.11	0.80	0.14
13.0	0.06	0.39	0.06	0.49	0.08
15.0	0.01	0.15	0.02	0.20	0.03

Table 3 contains the intra-correlation energies obtained using the IEPA, CEPA2 and PNOCI schemes, as well as the CEPA2 and PNOCI intra-correlation energies obtained when omitting the effect of intra-inter coupling on this term. A comparison of the coupled and uncoupled intra-correlation energies shows that intra-inter coupling provides most of the intra repulsion for  $R > 5.0$  a.u. and a diminished but significant amount, on a relative basis, for  $R \leq 5.0$  a.u. This repulsion is due to the exclusion effect caused by orbital overlap at small  $R$ , and by induced polarisation at large  $R$ , which also diminishes the total intra-atomic correlation contributions.

The intra-correlation energy contribution included in the inter-intra coupling term is approximately exponential in nature. Thus, it can be absorbed in damping functions in semi-empirical models employing a van der Waals expansion to describe the dispersion or inter-correlation energy since such damping functions generally contain an exponential component. The non-exponential component of the intra-correlation energy is rather small compared with the other contributions to the total interaction energy.

At  $R = 2.0$  a.u. the intra-correlation energy contribution through coupling in the CEPA2 result deviates from the general exponential nature of this term and is smaller than expected. This is not observed in the PNOCI calculation which, although based on natural orbitals obtained from the same IEPA calculation, differs from CEPA2 in that the orbitals have different coefficients, and the correlation energy due to coupled pairs (rather than renormalised pairs) is not taken into account. At such short distances, detailed analysis of the interaction contributions would require questioning the rigid rotor and simple representative geometry assumptions of the present work. However, the observed discrepancy in PNOCI and CEPA2 intra-correlation energies at  $R = 2.0$  a.u. indicates an increasingly important role of simultaneous double excitations to the overall correlation energy at very short intermolecular distances.

If we compare the coupled CEPA2 and PNOCI intra-correlation energies, the inclusion of quadruple excitations in the CEPA2 procedure reduces the restrictions placed on the electron distribution and leads to a less repulsive potential throughout the interaction domain sampled.

**Table 4. Inter-correlation energies ( $\mu$ h)**

$R$ (a.u.)	IEPA	CEPA2 $c$	CEPA2 $u$	PNOCI $c$	PNOCI $u$
2.0	-20450.05	-17976.66	-19774.44	-17435.16	-19690.77
3.0	-8786.09	-7646.82	-8365.47	-7370.80	-8348.57
4.0	-3418.06	-2966.62	-3226.86	-2847.11	-3224.15
5.0	-1275.60	-1098.81	-1196.30	-1049.74	-1195.91
5.5	-778.01	-666.36	-727.21	-635.11	-727.06
6.0	-478.22	-406.91	-445.49	-386.95	-445.43
6.5	-297.96	-251.78	-276.65	-238.94	-276.63
7.0	-189.00	-158.62	-174.94	-150.26	-174.94
8.0	-81.11	-67.22	-74.66	-63.51	-74.66
9.0	-38.10	-31.27	-34.92	-29.50	-34.92
10.0	-19.47	-15.87	-17.78	-14.95	-17.78
11.0	-10.75	-8.74	-9.81	-8.23	-9.81
12.0		-4.98	-5.64	-4.69	-5.64
13.0	-3.79	-3.06	-3.43	-2.88	-3.44
15.0	-1.57	-1.27	-1.42	-1.19	-1.43

A comparison of the present CEPA2 intra-correlation energy (which includes the effects of inter-intra coupling) with those obtained from the 78 function basis set at  $R = 4.0$ , 6.5 and 9.0 a.u. gives energies of 404.04, 25.28 and 3.48  $\mu$ h versus 382.06, 24.46 and 3.16  $\mu$ h respectively. The differences in

energy are probably due to replacement of the bond functions in the smaller basis by nuclear centred functions, intended to improve the description of the inter-correlation energy.

Inter-correlation energies, obtained from the IEPA, CEPA2 and PNOCI schemes, as well as the uncoupled CEPA2 and PNOCI energies, are given in Table 4. By taking the coupled CEPA2 energy as being the most accurate, then at  $R=6.5$  a.u. omission of the intra-inter coupling leads to an overestimation of the attraction by about 9.9%. Omission of the quadruple excitations in the PNOCI scheme underestimates the attraction by about 5.1% and the IEPA scheme, which uncouples the intra- and inter-correlation energies as well as the inter singlet and triplet pairs, overestimates the attraction by about 18%.

Comparing the CEPA2 inter-correlation energies for the present and 78 function basis at  $R=4.0, 6.5$  and  $9.0$  a.u. gives values of  $-2966.62, -251.78$  and  $-31.27 \mu\text{h}$  versus  $-2858.30, -230.09$  and  $-26.39 \mu\text{h}$  respectively. Thus, a significant improvement was made in describing the attractive region of the potential, and the repulsive wall was made a little softer.

**Table 5. Comparison of potentials**

R (a.u.)	Energy ( $\mu\text{h}$ )	
	Present	Buck <i>et al.</i> (1983)
2.0	193947.91	179903.99
3.0	42948.95	35985.79
4.0	7574.59	5777.37
5.0	890.95	594.53
5.5	176.26	78.83
6.0	-54.57	-78.84
6.5	-104.15	-107.15
7.0	-97.23	-94.59
8.0	-54.89	-54.09
9.0	-28.21	-27.99
10.0	-14.72	-14.61
11.0	-8.11	-8.02
12.0	-4.61	-4.64
13.0	-2.82	-2.81
15.0	-1.14	-1.16

Rather than comparing the present potential with a large number of  $\text{H}_2\text{-H}_2$  isotropic potentials, which differ in their abilities to predict a wide range of experimental data anyway, a comparison will primarily be made with the potential of Buck *et al.* (1983). This potential was recently recommended in a study by Norman *et al.* (1984) for its ability to produce both solid state and scattering data. Thus, assuming both that the experimental data the potential can predict are correct and that the mathematical treatment used to derive the data from the simulated two-body potential is correct, the experimentally sampled repulsive region of this potential should be reasonably close to exact. The long range region of this potential is defined by a damped van der Waals expansion. As such it has the correct asymptotic behaviour and should



provide at least a smooth transition between the long range and repulsive regions, thereby giving a reasonable description of the shape and depth of the potential well.

Comparison of the present CEPA2 potential with that of Buck *et al.* (1983) in Table 5 shows that there is close agreement in the long range region, as expected. The present supermolecule calculations are in close agreement with a van der Waals expansion based on the accurate coefficients of Meyer (1976), and the Buck *et al.* (1983) potential is modelled on such an expansion at long range.

For  $R < 10.0$  a.u. the unmodified van der Waals expansion begins to degrade significantly in describing the attractive component of the interaction. The present supermolecule calculations determine the attractive component directly. The damped van der Waals expansion employed in the Buck *et al.* (1983) potential is in close agreement with the present results.

At  $R = 6.5$  a.u., near the potential minimum, the potential of Buck *et al.* (1983) is more attractive by about  $3 \mu\text{h}$  (about 2.9%). This difference is consistent with the attractive component the present potential is missing due to the CEPA2 neglect of triple excitations, based on the calibration of the CEPA2 method to full CI results. Including the effects of triple excitations would thus decrease the difference in the respective  $\epsilon$ ,  $R_m$  and  $R_0$  values obtained from theory (present work) and experiment (Buck *et al.* 1983).

Up to this point, the agreement between the two potential functions can be considered good. Small differences in the interaction energies of Table 5 can be attributed to approximations inherent in the present work (i.e. the use of a finite basis set, limitations in the CEPA2 procedure in accounting for all the available correlation energy and the use of one conformation to approximate the  $V_{000}$  isotropic interaction) and the approximations inherent in using a damped van der Waals expansion to describe the attractive component of the Buck *et al.* (1983) potential (i.e. the correct method and extent of damping is not known).

In the repulsive region, the potential of Buck *et al.* (1983) is less repulsive than the present potential. At  $R = 4.0$  a.u., for example, the interaction energies are  $5777.37$  and  $7574.59 \mu\text{h}$  respectively, a difference of  $1797.22 \mu\text{h}$ .

All of this difference cannot be due to basis incompleteness. In going from the 78 function basis to the present 102 function basis the SCF energy improved by only  $15.28 \mu\text{h}$  (0.15% of the SCF interaction energy) and the total interaction energy by  $101.63 \mu\text{h}$  (1.3% of the total interaction energy) at this point. The larger change in the total interaction energy was achieved by mainly improving the inter-correlation energy in going from a basis set with only one d function midbond to the present basis. Increasing the present basis set would not result in changes to the potential as large as above since the scope for improving H<sub>2</sub> polarisabilities has now been substantially diminished.

Further, the energy difference cannot be due to the incompleteness of the CEPA2 method alone since this would require an improvement of about 70% in the correlation energy. We consider CEPA2 correlation energies in these weakly coupled pair interactions to be no more than about 3% in error, based on the full CI calibration. Even allowing for a 5% error in the CEPA2

inter-correlation energy, the potential would only change by about 2% ( $148 \mu\text{h}$ ) at this point instead of the required 24%. This is because the interaction energy in the repulsive region is dominated by the SCF energy, with this dominance increasing with decreasing  $R$ .

Finally, approximating the  $V_{000}$  term by the  $\text{DD}^1$  conformation was seen to underestimate the repulsion by about 2.7% or  $198 \mu\text{h}$ , compared with a four term approximation when using the IEPA method at this point ( $R = 4.0 \text{ a.u.}$ ). The single geometry approximation would thus compensate the basis set and CEPA2 deficiencies to some extent, thereby slightly decreasing the discrepancy between theory and experiment.

In view of these comments, it is difficult to see how any *ab initio* calculation can reproduce the repulsive part of the potential of Buck *et al.* (1983). The Buck *et al.* (1983) potential can describe their scattering data, as well as the solid state data, and it seems improbable that the data from two different types of experiments have similar errors. It is therefore concluded that separate inversion of the molecular beam and solid state experiments does not lead to an effective two-body isotropic potential for this interaction, in regions of the potential they are supposed to effectively sample. The reasons for this involve questioning the contribution of three-body effects in the experimental results, the statistical sampling of the various angular terms in the experiments, and the accuracy of inversion techniques used in reducing experimental results to a two-body isotropic potential.

At this stage, two factors need to be stressed. Firstly, the disagreement between theory and experiment in the repulsive region of the potential is not primarily due to how the electron correlation energy was taken into account. In the repulsive region, the SCF energy dominates and any reason for disagreement with experiment involves a brave questioning of the SCF formalism if theory is thought to be in error.

Secondly, the disagreement between theory and experiment is by no means limited to the Buck *et al.* (1983) potential. Their potential was chosen for comparison because it is the most recent and probably the best experimentally derived potential available for the present interaction. The potentials of Silvera and Goldman (1978), McConville (1981), Ross (1974) and Goldman (1976) are also significantly more attractive in the repulsive region than the present, whereas the potential of Bauer *et al.* (1976) is significantly more repulsive in this region.

The difference in descriptions of the repulsive wall by potential functions obtained from the more precise scattering or solid state experiments or the more precise theoretical studies is not limited to the present interaction (Senff 1987).

Experimental verification of the reliability of the present computational approach has been obtained by Larsen *et al.* (1988) in a study of the  $\text{He-Li}^+$  interaction through ion mobility studies!

#### 4. Conclusions

The present study has shown that a close approximation to the isotropic  $\text{H}_2\text{-H}_2$  interaction can be obtained by selecting one representative geometry to

model the potential function. Calculations using a smaller basis set were used to determine which geometry would be suitable by comparing an angular average to  $V_{000}$  in regions dominated by different intermolecular forces with those obtained by the representative conformation. A comparison of these results gives a good indication of the errors involved in using this approximation. By using a large basis set to model this interaction and a computational formalism whose performance has been checked against a full CI calculation, it is possible to obtain good estimations of the errors inherent in the present calculations.

A comparison of the present results with  $V_{000}$  potential functions obtained from experimental data shows that most of the experimentally derived potentials are significantly softer in the repulsive region than the present. The difference lies outside any conceivable error bars of the present work. It therefore appears that the differences could be due to the inversion of experimental data to give a two-body potential function. This possibility is reinforced by the close agreement obtained between a similar study of the He-Li<sup>+</sup> system (Senff and Burton 1986) and that from recent mobility studies (Larsen *et al.* 1988), while the beam data again led to significantly different potential functions.

Our presentation of the various contributing components of the total interaction energy in the present work should be of use in semi-empirical work, which is currently necessary for providing potential functions between larger interacting systems beyond the present possibility of accurate *ab initio* work using conventional approaches.

## References

- Ahlrichs, R., Lischka, H., Staemmler, V., and Kutzelnigg, W. (1975a). *J. Chem. Phys.* **62**, 1225.  
Ahlrichs, R., Driessler, F., Lischka, H., and Staemmler, V. (1975b). *J. Chem. Phys.* **62**, 1235.  
Bauer, W., Lantzsche, B., Toennies, J. P., and Walaschewski, K. (1976). *Chem. Phys. Lett.* **17**, 19.  
Boys, S. F. (1960). *Rev. Mod. Phys.* **32**, 296.  
Boys, S. F., and Bernardi, F. (1970). *Mol. Phys.* **19**, 553.  
Buck, U., Huisken, F., Kohlhasse, A., Otten, D., and Schaefer, J. (1983). *J. Chem. Phys.* **78**, 4439.  
Burton, P. G. (1983). *Chem. Phys. Lett.* **100**, 51.  
Burton, P. G., and Senff, U. E. (1982). *J. Chem. Phys.* **76**, 6073.  
Burton, P. G., and Senff, U. E. (1983). *J. Chem. Phys.* **79**, 526.  
Goldman, V. V. (1976). *J. Low. Temp. Phys.* **24**, 297.  
Harrison, R. J., and Handy, N. C. (1983). *Chem. Phys. Lett.* **98**, 97.  
Huzinaga, S. (1965). *J. Chem. Phys.* **42**, 1293.  
Koide, A., and Kihara, T. (1974). *Chem. Phys.* **5**, 34.  
Larsen, P.-H., Skullerud, H. R., Lovaas, T. H., and Stefansson, Th. (1988). *J. Phys. B* **21**, 2519.  
McConville, G. T. (1981). *J. Chem. Phys.* **74**, 2201.  
Maeder, F., and Kutzelnigg, W. (1976). *Chem. Phys. Lett.* **37**, 285.  
Meyer, W. (1971). *Int. J. Quant. Chem. Symp.* **5**, 59.  
Meyer, W. (1973). *J. Chem. Phys.* **58**, 1017.  
Meyer, W. (1976). *Chem. Phys.* **17**, 27.  
Norman, M. J., Watts, R. O., and Buck, U. (1984). *J. Chem. Phys.* **81**, 3500.  
Ross, M. (1974). *J. Chem. Phys.* **60**, 3634.  
Senff, U. E. (1987). Ph.D. Thesis. Univ. Wollongong.  
Senff, U. E., and Burton, P. G. (1985). *J. Chem. Phys.* **89**, 797.  
Senff, U. E., and Burton, P. G. (1986). *Mol. Phys.* **58**, 637.  
Silvera, I. F., and Goldman, V. V. (1978). *J. Chem. Phys.* **69**, 4209.

- Taylor, P. R., Bacskay, G. B., Hush, N. S., and Hurley, A. C. (1976). *Chem. Phys. Lett.* **41**, 444.  
Taylor, P. R., Bacskay, G. B., Hush, N. S., and Hurley, A. C. (1978*a*). *J. Chem. Phys.* **69**, 1971.  
Taylor, P. R., Bacskay, G. B., Hush, N. S., and Hurley, A. C. (1978*b*). *J. Chem. Phys.* **69**, 4669.  
Taylor, P. R., Bacskay, G. B., Hush, N. S., and Hurley, A. C. (1979). *J. Chem. Phys.* **70**, 4481.

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