Journal of Physical & Theoretical Chemistry
Islamic Azad University of Iran 4 (1)
(2007)
Science and Research Campus
ISSN: 1735-2126

High level Ab inito bench mark computaions on weak interactions $(H_2)_2$ dimer revisited

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ABSTRACT

The Potential Energy Surface PES of $(H_2)_2$ dimer has been investigated, using five simple rigid rotor models. These models are called: head to head, symmetric side to side, L , steplike and T model. All calculations were done at two levels of ab initio methods: MP2(Full) and QCISD (T,Full) using cc-pVTZ basis set at singlet state of spin multiplicity. The results of scanning PES were then fitted to Taylor series up to 15 terms to obtain the equilibrium distances and interaction energies between pairs of H_2 molecules.The standard deviation of the residuals in fitting procedure is well below 10^{-9} in all cases.L model has been found to be the most stable one instead of previously reported T model and 7 times more stable than other models.The validity of hard sphere approximation was also tested by solving simple mathematical equation and found to be no longer valid in these interactions.

Keywords: $(H_2)_2$; PES ; Rigid Rotor ; Taylor Series ; QCISD(T) ; L model

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INTRODUCTION

The PES of H_2 dimers has been investigated with various abintio methods and basis stes[1-5].This PES with 4 electrons and 4 nuclei , is not only suitable for doing High level compuations to test the simple approximations like rigid rotors and hard spheres , in reasonable computation time but also the best one for examining the accuracy of theoretical methods in computing the weak interactions[6-12].Refering to some recent results, Røeggen and Wind have done several calculataions based on geminal model and uncontracted gaussian type basis sets,they found that "T" structure is the global minimum of the potential among their rigid rotor models [13-15].Diep and Johnson have done a series of calculations using CCSD(T) ab initio method with aug-cc-pVnZ(n=2,3,4) basis sets and using many configurations of $(H_2)_2$ dimer. They reported a well depth of less than –50K (158 μhartree) for "T" structure [16-18].

This PES has been revisited in this work with including new rigid rotor model , called , L model and increasing the points of calculations as well as the curve fitting precission.

Computational Details

Equilibrium bond length and total energy of H_2 have been calculated at MP2 (All electrons) and QCISD (T) (All electrons) using cc-pVTZ basis set. These values are gathered in Table1. Five rigid rotor models have been constructed based on H_2 equilibrium bond length at each level , theses are depicted in Fig.1.

The chosen scan interval values for R, were 0.1 A^0 to 4.1A^0 (step size 0.02A^0) in all models at each level , except symmetric side to side and step like , which the interval has been expanded to 6.0A^0 to detect the potential energy well . For reducing the numerical errors in binding energy calculations, the energies of scan points were used with at least 11 decimals .All points were corrected via BSSE computations for obtaining interaction energies , E_{int}(R).Ab initio Computations have been performed using Gaussin98(Rev A.6) [19] . Fit1D code has been used for fitting the PES to Taylor series[20].

RESULTS AND DISCUSSION

The equilibrium value of R (R_e) and its related binding energy (E_{int}(R) or U_0) , have been determined using Taylor series with 15 terms , corresponds to polynomial of degree14, Eq.1.

$$E_{int}(R) : \sum_{n=0}^{n=14} u_n (R - R_e) \qquad \textbf{(Eq.1)}$$

Generally the lowest fitting error has been obtained using the points from 2.0 A^0 . R_e , U_n and error values have been gathered in Table 2-3 for each method and each model. According to these tables both SSR and SDR are well below 10^{-9} , which 1000 times smaller than U_0 , indicating the very accurate fitting. Both MP2 and QCISD(T) predicted the same order of R_e :

Symmetric side to side > step like > head to head > L = T model

The greatest difference between the R_e values at MP2 and QCISD(T) was found in head to head model (0.14 A^0) and the least for L model (0.04 A^0) which can be attributed to the MP2 deficiency in estimating the very weak interactions (about 10 μh) in comparison to QCISD(T) /cc-pVTZ level which is near the exact solution of Schrödinger equation. Based on the results of former level (Table3) , the value of -79.5 μh is reported for the interaction energy of two H_2 molecule in L and -77.0 μh for T model. The precision of curve fitting (10^{-9} h) allow us to establish the L model as the lowest energy model. With the same reasoning , step like and head to head models predicted to have the same amount of stability. They are 6 μh more stable than side to side model.

At MP2(Table2) , the difference of the interaction energy between L and T model is only 0.48 μh with the latter found to be more stable in agreement with QCISD(T) results. While MP2 predicts that the step like model is 3.5 μh more stable than head to head , QCISD(T) predicts the same amount of interaction energy for both (Based on fitting error). Head to Head model is predicted to be 1.5 μh more stable than side to side in QCISD(T).

The other part of this discussion will be spent for deriving the value of R in which E_{int}(R) is equal zero. According to. Lennard-Jones's idea this R value can be assigned to the size of molecule. The R values (R^0) , derived from solving Eq.2 are gathered in Table 4.

$E_{int}(R)= \Sigma u_n (R-R_e)^n = 0$ (n=0,1,2,3,…,14) **(Eq.2)**

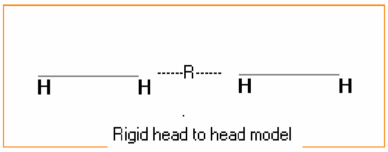
This table demonstrates that the size of molecule(as LJ proposed in the context of Hard sphere interactions) is highly depends to the spatial orientations which the two molecules mutually interact(Min: 2.4 A^0 , Max :3.6 A^0). There exist two points in the graph of $E_{int}(R)$ which this value is equal to zero. One at R^0 , the other at infinity. Although the interaction energy in both points is zero but the total force (the slope of the curve) is not zero at R^0. This net unbalanced force is the deriving force for reaching to the equilibrium (where the net force acting within molecule is zero). This analysis implies that the Energy is not the sole key quantity in studying the molecular properties. The Forces within molecules also plays crucial rule in the molecular properties. So both of them should be used when one intends to study the chemical properties of molecules.

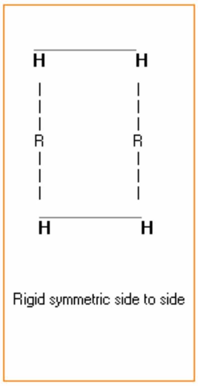
CONCLUSIONS

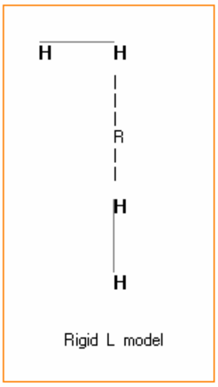
Five rigid rotor based models of interaction have been proposed for the two H_2 molecules. These were called : Head to Head , Step like , Symmetric Side to side , L and T models. BSSE corrected interaction energy , $E_{int}(R)$, was calculated at both MP2(Full) and QCISD(T, Full) with cc-pVTZ basis set for each of the cited model. The PES was then fitted to the Taylor series of expansion up to 15 terms (degree of 14) for computing the equilibrium values of R and well depth (U_0). The results of two ab initio methods have been compared with each other. Both methods predicts that L model is the most stable form of interaction and symmetric side to side the leats. Based on LJ idea of hard sphere interaction , the value of R^0 , at which the interaction energy becomes zero , was calculated for each model. The large range of R^0 (1.2 Å at QCISD(T,Full)) values are found to be incantatory to the simple hard sphere approximation.The crucial rule of the Forces acting within molecules (the slope of Energy profile) in the study of Intermolecular interactions is once again addressed.

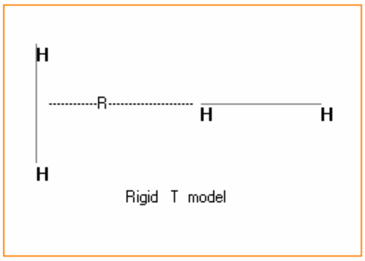
Acknowledgments

A.Sadjadi is grateful to professor Kirk A.Peterson for accessing his useful fitting program and his helpful comments.









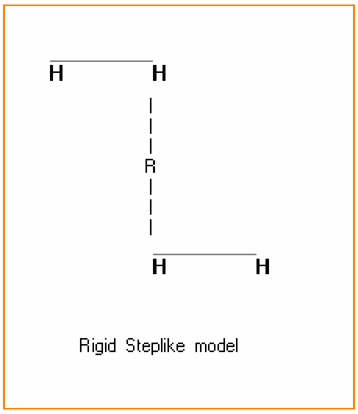


Fig.1. Five rigid rotor models. R is the variable parameter for searching the PES.In T model , one H_2 molecule close to other in the perpendicular direction which passes through the mid point of the bond length of the former.

Table1. Equilibrium bond length and energy for H_2 molecule

Parameters	**MP2**	**QCISD(T)**
Bond length[*]	0.73701659	0.74262857
Total energy[**]	-1.1646497775295	-1.1723366890

*values are given in A^0 (for singlet electronic state)

** values are given in a.u and without ZPE correction.

Table2. Fitting parameters at MP2(Full)/cc-pVTZ level.

Parameters[*]	**Head to Head**	**Symmetric Side to Side**	**Step like**	**L model**	**T model**
$\mathbf{U_0}$	**-.0000087070**	**-.0000072050**	**-.0000121913**	**-.0000700503**	**-.0000695690**
U_1	.504622E-20	.905108E-22	.937583E-22	.275840E-19	-.404327E-20
U_2	.0000322847	.0000233703	.373684E-04	.0001688615	.0001725205
U_3	-.0000564909	-.0000434133	-.666670E-04	-.0002633564	-.0002840908
U_4	.0000561902	.0000462856	.677314E-04	.0002366225	.0002714276
U_5	-.0000393699	-.0000348743	-.486118E-04	-.0001717828	-.0001919788
U_6	.0000210515	.0000202824	.264902E-04	.0001217412	.0001128914
U_7	-.0000149694	-.0000094238	-.108916E-04	-.0000633378	-.0000570870
U_8	.0000115186	.0000033044	.346490E-05	.0000073361	.0000277690
U_9	.0000077280	-.0000009363	-.138430E-05	-.0000019588	-.0000153329
U_{10}	-.0000059963	.462725E-06	.803746E-06	.0000119744	.199788E-06
U_{11}	-.0000171653	-.265354E-06	-.263272E-06	.0000021122	.768012E-05
U_{12}	.0000009754	.570083E-07	-.124534E-07	-.485053E-05	.502514E-06
U_{13}	.0000102706	.959170E-08	.287173E-07	-.178206E-05	-.255757E-05
U_{14}	.0000034932	-.396333E-08	-.492259E-08	.220140E-06	-.715101E-06
$\mathbf{R_e}$[*]	**3.439155497**	**4.113908786**	**3.909708864**	**3.256459367**	**3.257363513**
SSR[**]	4.888E-18	6.870E-16	5.891E-16	7.688E-18	4.945E-19
SDR[***]	2.147E-10	1.853E-09	1.716E-09	2.693E-10	6.830E-11

*All "U" values are printed in atomic units, "R" values are printed in A^0 .

** Sum of squares of residuals.

***Standard deviation of the residuals

Table3. Fitting parameters at QCISD(T, Full)/cc-pVTZ level.

Parameters[*]	**Head to Head**	**Symmetric Side to Side**	**Step like**	**L model**	**T model**
U_0	**-.0000171317**	**-.0000114594**	**-.0000171322**	**-.0000795469**	**-.0000769505**
U_1	.489501E-20	-.189763E-23	-.788418E-21	-.572289E-20	.174176E-19
U_2	.0000542840	.0000352527	.0000505421	.0001931060	.0001929670
U_3	-.0000931475	-.0000642800	-.0000887826	-.0003002696	-.0003181583
U_4	.0000928374	.0000670072	.0000886860	.0002730420	.0003040349
U_5	-.0000669650	-.0000493477	-.0000625467	-.0002036078	-.0002148459
U_6	.0000332554	.0000283986	.0000335417	.0001392275	.0001260124
U_7	-.0000196647	-.0000131858	-.0000136490	-.0000628146	-.0000647676
U_8	.0000275369	.445567E-05	.442909E-05	.758253E-05	.0000332131
U_9	-.471163E-05	-.119256E-05	-.189944E-05	-.0000100048	-.0000169353
U_{10}	-.0000179131	.710243E-06	.109340E-05	.0000134090	-.114851E-05
U_{11}	-.564085E-05	-.431872E-06	-.323914E-06	.0000055695	.795265E-05
U_{12}	.708971E-05	.774754E-07	-.369911E-07	-.537884E-05	.464869E-06
U_{13}	.531747E-05	.235043E-07	.432366E-07	-.210581E-05	-.226134E-05
U_{14}	.109930E-05	-.743458E-08	-.694132E-08	.478227E-06	-.475498E-06
R_e[*]	**3.294568512**	**4.004911864**	**3.823523279**	**3.213385552**	**3.220312994**
SSR[**]	2.749E-16	1.319E-15	5.837E-16	9.985E-18	9.972E-19
SDR[***]	1.610E-09	2.568E-09	1.708E-09	3.069E-10	9.699E-11

*All "U" values are printed in atomic units, "R" values are printed in A^0 .

** Sum of squares of residuals.

***Standard deviation of the residuals

Table4. R^0 values at both MP2(Full) and QCISD(T,Full) methods.

Model	**Head to Head**	**Side to Side**	**Step like**	**L**	**T**
MP2	3.068	3.731	3.515	2.812	2.468
QCISD(T)	2.901	3.613	3.421	2.770	2.424

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