Theoret. Chim. Acta (Berl.) 41, 89–91 (1976)

Short Communications

Ab initio Crystal Orbital Studies on Linear Chains of H Atoms

Miklos Kertesz

Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest

Jože Koller and Andrej Ažman

Chemical Institute Boris Kidrič, University of Ljubljana

Received July 7, 1975

An *ab initio* crystal orbital method is used to calculate the energies of an infinite chain of H atoms and of linear arrangements of H_2 molecules with different interatomic distances. The H_2 arrangements are not stable in respect to isolated molecules. The cohesive energy of an optimized arrangement of H atoms chain is 0.0354 a.u.

Key words: H chains, crystal orbital study of ~

Crystal orbital calculations of an infinite chain of H atoms have been reported several times [1–3] but only with the equidistant H atoms. The *ab initio* work of Harris *et al.* [4] in three dimensions used the crystal orbital of a modified Bloch type. A number of *ab initio* calculations on H atom clusters have been done, the most extended one being due to Krislow *et al.* [5]. The purpose of this note is to present the results of the calculation with the *ab initio* crystal orbital method [6] using Bloch type wave functions. The basis set we have used is a 1*s* Slater orbital with exponent 1.13 expanded into four Gaussian functions [7]. The energy of H atom is in this approximation -0.49008 a.u. The calculations have been done on two linear arrangements of H atoms: metallic type chain with equidistant H atoms and on the one dimensional model of molecular crystal composed of H_2 molecules. In metallic chain with one H atom in unit cell the calculation has been extended over 16 neighbours. In Table 1 also the energy per H atom is given as resulted from *ab initio* calculation on the cluster of 30 H atoms. The energy per atom has minimum at 1.88 a.u. for both methods but this energy is overestimated with cluster type calculation except at large interatomic distances. At $R = 1.88$ a.u. two calculations were done with the extended basis set 4–31 *G* [8]. In the first one standard exponents have been used and the energy of H atom is -0.49823 a.u. In the second one the optimized exponents were determined with the energy of H atom of -0.49868 a.u. As is known if a one dimensional system contains a partly filled band it is common to obtain besides the symmetric solution also the broken symmetry one [9]. The latter type of solution could be found when the elementary

Table 1. The energy (a.u.) per atom for chain of H atoms obtained with cluster (CC) and crystal orbital (CO) calculation and with broken symmetry solution (BS)

R(a.u.)	CC	CO	BS
1.7	−0.51521	−0.47597	−0.48042
1.88	−0.52912	−0.52787	−0.52955
1.886	−0.52912	−0.52787	
2	−0.52783	−0.52680	−0.52741
4	−0.42409	−0.42790	
1.88		−0.53347[a]	
1.88		−0.53406[a]	

[a] Extended basis set.

Table 2. Energy (a.u.) per atom for molecular crystal H_2 by cluster (CC) and crystal orbital (CO) approach

D_1 (a.u.)	D_2(a.u.)	CC	CO
1.88	1.92	−0.53039	−0.52964
1.88	2	−0.53223	−0.53147
1.88	2.1	−0.53430	−0.53360
1.88	2.4	−0.53904	−0.53854
1.88	2.8	−0.54277	−0.54249
1.45	1.92	−0.53465	−0.53146
1.45	2.4	−0.54905	−0.54649
1.45	6.5	−0.56124	−0.56124
1.88[a]		−0.54706	
1.45[b]		−0.56126	

[a, b] Results of H_2 molecule.
[b] Optimized distance of H_2 molecule.

cell was enlarged to two H atoms in unit cell. The hydrogen chain becomes in this case an insulator with an energy gap of 0.229 a.u. at $R=1.88$ a.u. This broken symmetry solution which is of bond order alternation type lowers the energy per H atom indicating that an alternating arrangement will be more stable. The calculations on a one-dimensional model for H_2 molecular crystal (Table 2) have been done at few values of D_1 (distance between H atoms) and D_2 (distance between H_2 molecules) with one H_2 molecule in unit cell with 16 atomic neighbours interactions. The results show that the molecular crystal is stable to H atom dissociation but is not stable to H_2 molecule dissociation.

The calculated equilibrium distance and the energy per atom for the H atomic chain with symmetric solution are in agreement with the cluster calculation of Krislow *et al.* [5] and with the results of Berggren and Martino [1]. The equilibrium distance $R=1.88$ a.u. is almost equal to that reported by Krislow *et al.* and the cohesive energy (difference between energy per atom and the energy of H atom) is 0.037 a.u. (minimal basis set) or 0.0352 a.u. and 0.0354 a.u. (extended basis set). The values given by Krislow *et al.* and Berggren and Martino are 0.033 a.u. and 0.01 a.u. respectively.

Acknowledgements. This work was supported by the Boris Kidrič Fund. We would like to thank Dr. E. Zakrajšek for his excellent eigenvalue program.

References

1. Berggren,K.F., Martino,F.: Phys. Rev. **184**, 484 (1969)
2. Calais,J.L.: Arhiv Fysik **28**, 511 (1965)
3. André,J.M.: J. Chem. Phys. **50**, 1536 (1969)
4. Harris,F.E., Monkhorst,H.J.: Phys. Rev. Letters **23**, 1026 (1969)
5. Krislow,D.H., McKelvey,J.M., Bender,C.F., Schaefer,H.F.: Phys. Rev. Letters **32**, 933 (1974)
6. Del Re,G., Ladik,J., Biczó,G.: Phys. Rev. **155**, 997 (1967)
7. Hehre,W.J., Stewart,R.F., Pople,J.A.: J. Chem. Phys. **51**, 2657 (1969)
8. Dietchfield,R., Hehre,W.J., Pople,J.A.: J. Chem. Phys. **54**, 724 (1971)
9. Kertesz,M.: Phys. Stat. Solidi (b) **69**, K141 (1975)

Dr. A. Ažman
Department of Chemistry
University of Ljubljana
61001 Ljubljana P.O.B. 537
Yugoslavia