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Nonadditive Interaction in Molecular Hydrogen at High Pressure*

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Ab initio quantum-mechanical calculations have been carried out for the pair and triplet potential energies of hydrogen molecules in order to check the pairwise additivity assumption in interpreting the shock experiments of van Thiel *et al.* It is shown that this assumption fails at distances less than 4.5 bohr. An effective pair potential obtained from the present calculations compares favorably with experimentally determined pair potentials at 3.5 bohr or larger. At shorter distances, it shows the presence of higher-order many-body forces.

Nearly all statistical mechanical calculations which have been carried out to date depend on an important assumption: Intermolecular forces of N molecules can be sufficiently well approximated by the sum of interactions taking place between $N(N-1)/2$ individual pairs. A well-known exception is the nonadditive triple-dipole ("Axilrod-Teller") force,¹ but it exists at large intermolecular separations and is relatively small. At shorter distances, the nonadditivity^{2,3} should also occur as a direct consequence of the Pauli principle which requires the charge cloud of two molecules to be altered in the presence of a third molecule. The purpose of this Letter is to report *ab initio* three-body energy calculations for molecular hydrogen.

Only a small number of electrons need be considered in the case of H_2 . Hence, very precise theoretical results can be obtained. The results are especially interesting since they can be compared with available high-pressure measurements on hydrogen and deuterium.^{4,5} The most recent additions to these are the experiments of van Thiel *et al.*,⁶ who achieved a pressure of 880 kbar by shock compressing D_2 sevenfold from normal liquid density, and of Grigor'ev *et al.*,⁷

who estimated that a pressure of 8 Mbar was achieved by magnetically imploding liquid H_2 to a density 22 times the normal liquid density. Temperatures generated in both experiments were approximately 7000°K. High temperatures and high compressions achieved in these experiments make it possible to probe the intermolecular potential most effectively at short distances ranging down to 3 bohr (1 bohr = 0.5292 Å).⁶ Hence, the detailed theoretical calculations on hydrogen molecules would answer whether the heretofore elusive nonadditive many-body forces would be detectable or might even become dominant, bringing about a complete breakdown of the pairwise additivity assumption.

To investigate the possibility of nonadditive forces we selected a geometry of three H_2 molecules (A , B , and C) with the H_2 - H_2 center-to-center intermolecular distances (R) forming an isosceles triangle, $R_{AB} = R_{BC} \neq R_{AC}$. The H-H bond lengths are fixed at 1.4 bohr and their axes are restricted to lie perpendicular to the plane formed by the three centers (D_{3h} symmetry). Besides the triplet interaction, we have also examined interactions of two H_2 molecules (A and B), using four different geometries.^{8,9}

TABLE I. Pair (E_{AB}) and triplet (E_{ABC}) potentials of H_2 from SCF and CI calculations. Axes of H_2 are parallel to one another and perpendicular to the lines joining the molecular centers.^a

Types of calculations Calc. no.	$(N, R_{HH}, \text{config.})^b$	E_{AB} at $R_{AB} = 3$	
		SCF	CI
1	(5, 1.4, 247)	0.045379	0.040868
2	(11, 1.4, 671)	0.045166	0.039960
3	(5, 1.4, 1960)	...	0.040628
4	(5, R_{\min} , ^c 247)	0.044594	0.040489

Geometry ^d	E_{ABC} [$E_{ABC}/(E_{AB} + E_{AC} + E_{BC})$] (%)	
	SCF	CI
Equilateral triangle ($R_{AB} = R_{AC} = R_{BC} = 3$)	-0.023980 (-17.61)	-0.022002 (-17.95)
Linear equidistant ($R_{AB} = R_{AC} = 0.5R_{BC} = 3$)	0.004077 (4.49)	0.003865 (4.73)

^aEnergy unit is the hartree (27.21 eV) and distance unit is the bohr (0.5292 Å).

^b $N = 5$: two s and one set (p_x, p_y, p_z) of $2p$ functions per H; $N = 11$: five s and two sets of $2p$ functions. "Config." stands for the number of spin configurations included in the CI wave functions (C_{2v} geometry for calculations Nos. 1 and 4, D_{2h} symmetry for the other two calculations). The calculation No. 3 includes all configurations which could be constructed from the basis set $N = 5$. R_{HH} is the H-H bond length.

^c $R_{\min} = R_{HH}$ giving the minimum energy at fixed R_{AB} .

^dThese calculations are done by using $N = 5$, $R_{HH} = 1.4$, and config. = 894.

The pair (E_{AB}) and the triplet (E_{ABC}) potential energies are obtained by taking proper differences between the total ground-state energies of composite H_2 systems at geometries of interest and those for one or more molecules separated sufficiently far away. The computations for the ground-state energies were carried out by the configuration interaction (CI) method, using the iterative natural-orbital technique discussed elsewhere.¹⁰ The CI wave functions include the self-consistent-field (SCF) configuration plus all configurations arising from the replacement of at most two orbitals in the SCF configuration. As basis functions for the molecular orbitals, we chose five [two $1s$ and one set (p_x, p_y, p_z) of $2p$]

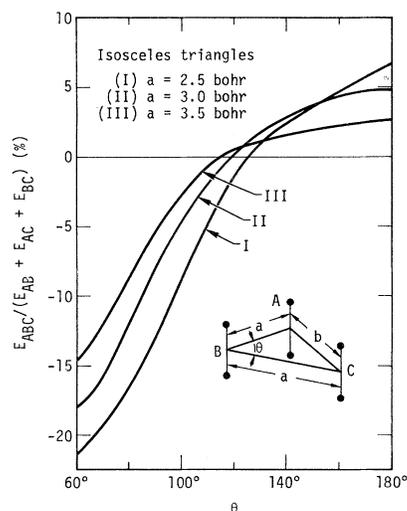


FIG. 1. Ratios (%) of the triplet potential energies to pair potential energies for $3H_2$.

functions per H atom, as was done previously.¹¹

The results of our calculations are summarized in Table I at selected geometries. Figure 1 shows the dependence of $E_{ABC}/(E_{AB} + E_{AC} + E_{BC})$ on the angle θ between R_{AB} and R_{BC} at fixed values of $R_{AB} = R_{BC}$. Table I shows that the electronic correlation included in the CI calculations lowers E_{AB} by about 10% from the SCF values. The differences in E_{ABC} between the SCF and the CI calculations are small. Note that the SCF and CI ratios $E_{ABC}/(E_{AB} + E_{AC} + E_{BC})$ are nearly equal in the case of the equilateral triangular geometry.

Sensitivities of the CI calculations to the number of basis functions, the number of configurations included, and the H-H bond length have been tested using $2H_2$ interactions. Table I shows the results of such tests at 3 bohr. We see that the various refinements do not affect the CI E_{AB} by more than 2%. This observation holds true also for the range (3 to 5 bohr) of R_{AB} and also for the other geometries that have been investigated here. General insensitivity of E_{AB} to parameter variations suggests that errors in the calculated E_{ABC} might also be insensitive.

The CI pair potentials for the four different geometries are combined into a spherically averaged form,⁹ which can be accurately represented by

$$E_{AB} = 3.536 \exp(-1.242R_{AB} - 0.06784R_{AB}^2), \quad 2.5 \leq R_{AB} \leq 4.5 \text{ bohr.} \quad (1)$$

At 7000°K (or $R \geq 3$ bohr),³ the spherical averaging should also be reasonable, i.e., our results show that the molecules are mostly freely rotating.

Figure 2 shows the theoretical pair potential, Eq. (1), and two effective pair potentials [$7.8 \exp(-1.7R) - 17R^{-6}$ and $8.2 \exp(-1.74R) - (13R^{-6} + 116R^{-8}) \exp(-400R^{-6})$] determined by Hoover *et al.*⁹ from the 214-kbar shock data.⁵ At $R_{AB} = 3$ bohr, we note that the theoretical E_{AB} is 0.0457 hartree, while the "experimental" potentials are 0.0228 and 0.0238 hartree. A similar analysis by Ross¹² on the 0.9-Mbar data⁶ indicates that the experimental potential could be as low as 0.018 hartree. The present *ab initio* E_{AB} is very unlikely to overestimate E_{AB} by such a large extent. It is also unlikely that electronic excitations, or dissociation to a sufficient extent, take place at 7000°K, accounting for the differences.

The possible three-body contribution to E_{AB} can be estimated from a theoretical "effective" pair potential E_{AB}^{eff} , which is evaluated by equating $\frac{12}{2} E_{AB}^{\text{eff}}$ (12 is the number of nearest neighbors) to the static lattice energy (U/N) of an H_2 crystal in fcc structure.¹³ That is, at each nearest-neighbor distance a ($\equiv R_{AB}$),

$$U/N = 6E_{AB}(a) + 3E_{AB}(\sqrt{2}a) + 12E_{AB}(\sqrt{3}a) + 6E_{AB}(2a) + 8E_{ABC}(a, a, a) + 12E_{ABC}(a, a, \sqrt{2}a) + 24E_{ABC}(a, a, \sqrt{3}a) + 6E_{ABC}(a, a, 2a) + \text{contributions by larger triplets}, \quad (2a)$$

$$U/N \equiv 6E_{AB}^{\text{eff}} + \text{contributions to } E_{AB}^{\text{eff}} \text{ at non-nearest-neighbor sites.} \quad (2b)$$

The triplet sum in Eq. (2a) contains only those triplets with the molecules A and C being the nearest neighbors to B . Included in the triplet interactions in U/N are those space orientations shown in Fig. 1. The other orientations are not considered here for an obvious computational difficulty of handling them. This may be one major source of error in the calculated U/N (see the next paragraph for a further discussion). It should, however, be noted that our main con-

clusions obtained from the present work will not be affected by it. Numerical values for E_{AB}^{eff} at $R_{AB} = 3, 3.5, 4,$ and 4.5 calculated in this manner lie, respectively, 89, 60, 47, and 35% below the theoretical E_{AB} ! They lie closer to the empirical pair potentials (see Fig. 2), differing at these distances by $-78, -16, +17,$ and 64% from the averages of the two empirical potentials. (The 64% deviation at 4.5 bohr quoted above amounts numerically to 0.00084 hartree. Such a small difference could be due either to an insufficient number of configurations included in our CI calculations, to inaccurate empirical data, or to both.)

In describing a highly compressed state of H_2 , we conclude, therefore, that (i) for $R_{AB} \leq 4.5$ bohr the additivity assumption becomes seriously in error, (ii) for $3.5 \leq R_{AB} \leq 4.5$ bohr inclusion of E_{ABC} is probably sufficient to take care of this, and (iii) for $R_{AB} < 3.5$ bohr further many-body (four- and more-body) contributions become increasingly dominant. At 2.5 bohr, for example, E_{AB}^{eff} calculated from Eq. (2) even gives a negative value (≈ -0.006 hartree), indicating that the higher-order effects should make a positive contribution. The E_{AB}^{eff} in Eq. (2b) includes only the nearest-neighbor contributions since, at the short R_{AB} that we are considering, E_{AB} is stiffly repulsive. Larger triplet configurations are not included in Eq. (2a), since E_{ABC} is an exponentially decreasing function of distance which decays exponentially faster than the decrease of E_{AB} . Hence, we expect that any further lowering of E_{AB}^{eff} on account of these corrections would amount to a small fraction of the contributions already included. In a more rigorous treatment,

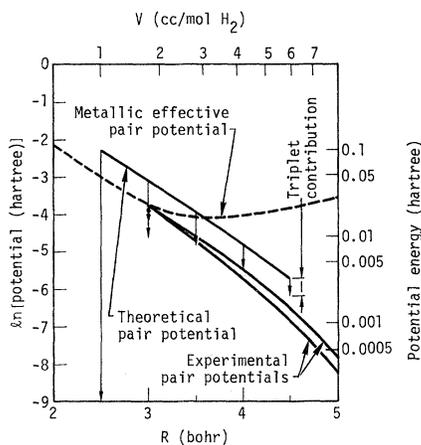


FIG. 2. Theoretical pair potential E_{AB} , Eq. (1). Further softening of E_{AB} by the triplet-potential contribution is indicated by downward vertical arrows. The shaded area is bracketed by two "experimental" pair potentials obtained from the 214-kbar data (Refs. 5 and 6). Double-headed arrow at 3 bohr indicates an additional lowering of the experimental pair potentials (Ref. 12) based on the 0.9-Mbar shock data (Ref. 6). The metallic pair potential (dashed) is obtained from Ref. 13. The scale at the top indicates the molar volume of H_2 in a close-packed lattice corresponding to the nearest-neighbor lattice spacing of R .

one might include different 3H_2 geometries besides those considered here. Any geometry which turns out to give a very repulsive E_{ABC} would be energetically excluded from significant occurrence in the crystal. Further physical justification for using the present 3H_2 geometry, besides its computational convenience, is based on the results of our 2H_2 calculations, which show the potential energies to be rather weakly dependent on the H_2 orientations, and on similar results obtained for another triplet geometry (i.e., equilateral triangles with coplanar H_2 axes pointing toward the center of the triangles). Our numerical values of E_{ABC} for $R_{AB} \leq 3$ bohr could change under a different set of approximations. The conclusions (i)-(iii), however, would likely remain valid.

A similar effective potential for metallic hydrogen (shown in Fig. 2) was obtained from the cohesive-energy expression of Neece, Rogers, and Hoover¹⁴ after subtracting the zero-point energy. The crossing point of the metallic and the molecular effective potentials in Fig. 2 gives the approximate location of the expected 0°K metal-insulator transition. Figure 2 shows that the crossing is not likely to occur for $R_{AB} \geq 3$ bohr. For $R_{AB} \leq 3$ bohr, many-body contributions become so large that no definitive conclusion as to the location can be drawn from the theoretical effective pair potential alone; the softening tendency of E_{AB}^{eff} , unless compensated by a much larger positive many-body force, would likely cause the transition pressure to move higher than the transition pressure of 2.8 Mbar at $R_{AB} = 3$ bohr obtained by the other workers.⁷ We plan to answer this by carrying out a finite-system quantum-mechanical calculation in the future.

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Thiel for explanation of his shock experiments. Details of the calculations on the H_2 potentials will be submitted for publication in due course.

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¹³A precise crystalline structure for a compressed molecular hydrogen phase is not experimentally known. We assume it, here, to be an fcc phase. This observation is based on an experimentally observed (α) molecular nitrogen phase at low temperatures. Energy differences between this structure and the other (β and γ) phases are typically negligible, amounting approximately to the 0° phase transformation energies. In most statistical-mechanical treatments an effective pair potential is assumed to be insensitive to thermodynamic phases. Note that this assumption has been used in the above discussion as well as in the case for comparing the present effective potential with those obtained in Refs. 6, 9, and 12.

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