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Short-range interaction between hydrogen molecules*

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Recent calculations of the ground-state energy of a system of four hydrogen atoms are reviewed from the point of view of discerning the short-range interaction potential between two hydrogen molecules. Consistency amongst the results of these calculations suggests that the potential for intermolecular separations in the region 1–2.5 Å can now be specified to about 10% with considerable confidence. Analytic fits to spherical averages of these results are presented. For calculations of properties of high-density solid molecular hydrogen, the bare pair potential may thus be regarded as well determined. The role of multicenter terms can then be examined; as for example, recent reported work seems to indicate that pairwise additivity is not altogether valid in practice.

I. INTRODUCTION

The purpose of this paper is to review recent calculations of the short-range, repulsive part of the interaction potential between two hydrogen molecules. Uncertainty in this portion of the potential has led to widely differing determinations of the equation of state for molecular hydrogen at very high pressures, and contributed to variations by more than an order of magnitude amongst predictions of the molecular to atomic phase-transition pressure.[1-10] We demonstrate in this review that recent calculations[11-25] of the short-range part of the potential are in sufficient agreement with each other as to suggest that this part of the potential may now be fairly well established. Unfortunately, there are still significant discrepancies with the limited experimental information available.[26-31] Most of the calculations that we discuss have appeared in the chemical physics literature, and many have been motivated by other concerns such as the four-center exchange mechanism between two impinging hydrogen molecules. Since this review is intended for a more general audience, we have included a brief description of the so-called *ab initio* techniques that have been used. It is not the purpose of this paper to give a complete review of the H_4 calculations, and we refer the reader to the paper by Rubinstein and Shavitt[18] for a more thorough list and discussion of the earlier efforts.

The organization of the paper is as follows. In Sec. II we describe the *ab initio* techniques, and in Sec. III the numerical results for the H_2-H_2 interaction energy that have been obtained with these methods. Possible analytic forms for the short-range part of the potential are discussed in Sec. IV. In Sec. V we comment on the applicability of these various results to calculations of the ground-state energy of molecular solid hydrogen. Finally, our summary is presented in Sec. VI.

II. MATHEMATICAL TECHNIQUES

We describe in this section the *ab initio* techniques by which the ground-state energy of a system of four hydrogen atoms has been determined.[11-25] It is customary to begin by making the Born-Oppenheimer approximation and neglecting any zero-point motion of the four nuclei. The nuclear position vectors $\vec{R}_A$, and thus the geometry of the system, are accordingly parameters in the problem. The desired energy is then the ground-state eigenvalue of the Hamiltonian

$$H=\sum_{A<B}\frac{1}{R_{AB}}+\sum_{i}\left(-\frac{1}{2}\nabla_i^{\,2}-\sum_{A}\frac{1}{r_{iA}}\right)+\sum_{i<j}\frac{1}{r_{ij}}\,, \tag{1}$$

where the indices A and i run over the four nuclei and four electrons respectively, $R_{AB}=|\vec{R}_A-\vec{R}_B|$, $r_{iA}=|\vec{r}_i-\vec{R}_A|$, and atomic units[32] have been used. The methods by which this energy has been approximately determined have in general been variational,[33] and thus have given upper bounds. These methods may be categorized according to the generality of the trial wave function used.

Heitler-London (HL)

The simplest calculation would appear to be a generalization of the well-known Heitler-London approach for the hydrogen molecule. In the case of four hydrogen atoms, one has

$$\psi_{\rm HL}=\tfrac{1}{2}[(a\bar{b}c\bar{d})-(\bar{a}bc\bar{d})-(a\bar{b}\bar{c}d)+(\bar{a}b\bar{c}d)]\,, \tag{2}$$

$$(a\bar{b}c\bar{d}) \equiv \frac{1}{\sqrt{4!}} \sum_{P} (-1)^{P} P[\chi(|\vec{r}_1-\vec{R}_a|)\chi(|\vec{r}_2-\vec{R}_b|)\chi(|\vec{r}_3-\vec{R}_c|)\chi(|\vec{r}_4-\vec{R}_d|)\alpha(1)\beta(2)\alpha(3)\beta(4)] , \tag{3}$$

$$\chi(r) \equiv (\zeta^3/\pi)^{1/2} e^{-\zeta r} . \tag{4}$$

As usual, the two spin functions are indicated by α and β. In Eq. (2), the bars placed over certain letters indicate the arrangement of the spin functions as shown in Eq. (3). The permutation operator P runs over all 24 permutations of four objects, and permutes both spatial and spin variables. Since it is presumed that the ground state will be an eigenfunction of the total spin with eigenvalue zero, it is necessary to combine four Slater determinants as is done in Eq. (2). This is a covalent (as contrasted to ionic) wave function, in that each of the four atomic orbitals (one centered on each nucleus) is singly occupied. If one substitutes Eq. (3) into Eq. (2), the spin functions may be grouped in the form of a singlet state for the electrons on nuclei a and b, multiplied by a singlet state for those on c and d. One considers this wave function to describe a state in which covalent bonds exist between atoms a and b, and between atoms c and d. It is possible to construct two more covalent wave functions, corresponding to bonds between other pairs of atoms, although only two of the three wave functions are linearly independent. The given geometric arrangement of the nuclei dictates which of the three (if any) is the best choice.

The Heitler-London wave function has no variational parameters (unless the effective nuclear charge ζ is varied), and so one must only evaluate

$$E_{\mathrm{HL}} = \frac{\langle \psi_{\mathrm{HL}} | H | \psi_{\mathrm{HL}} \rangle}{\langle \psi_{\mathrm{HL}} | \psi_{\mathrm{HL}} \rangle} . \tag{5}$$

The interaction energy between molecules may then be found by subtracting the energy of two isolated molecules—also calculated in the Heitler-London approximation. This is not a trivial exercise, for two reasons. The first is that for a general geometry, Eq. (5) involves some 64 distinct electron-nucleus attraction and electron-electron repulsion integrals.[34] Cancellation amongst these various terms results in the interaction energy being one or more orders of magnitude smaller than the size of some individual terms. Second, simple analytic expressions for the 39 three- and four-center integrals do not exist, and only in the last ten years have these integrals been accurately evaluated by rather elaborate computer programs.[35] In the early work, de Boer[36] neglected three- and four-center integrals altogether, while Evett and Margenau[37] and Mason and Hirschfelder[38] attempted to approximate them. Because of the extensive cancellation mentioned, such approximation schemes are not reliable. While giving reasonable dependence of the interaction energy on intermolecular separation, the calculations of de Boer and of Mason and Hirschfelder, for example, overestimate the orientation dependence by more than a factor of 2. We return to this point later.

Full configuration interaction

The two linearly independent covalent wave functions are referred to as configurations. Given our set of four atomic orbitals, one centered about each nucleus, it is also possible to construct 12 singly ionized configurations of the form

$$\psi_{\text{s.ion.}} - (1/\sqrt{2})[a\bar{b}c\bar{c}) - (\bar{a}bc\bar{c})] \tag{6}$$

and six doubly ionized configurations of the form

$$\psi_{\text{d.ion.}} = (a\bar{a}c\bar{c}) . \tag{7}$$

Each is a linearly independent wave function, satisfying the Pauli principle, and a spin-zero eigenfunction of the total spin. They correspond to the 20 possible ways of placing four indistinguishable electrons on four protons (using only 1s states) consistent with zero total spin.

A variational calculation of the ground-state energy in which the trial wave function is composed of a sum of these configurations, each multiplied by a variational parameter, is referred to as a "configuration-interaction" (CI) calculation. In a full configuration-interaction calculation, all configurations consistent with the geometric symmetry of the ground state are employed. To be more precise, the configurations referred to here are actually linear combinations of the original configurations which transform according to the appropriate irreducible representation of the point group of the four-atom system. Thus, for the linear geometry (see Fig. 1), only 12 (out of 20) configurations are needed.

A full CI calculation may be improved by enlarging the basis. So far, we have considered what is known as a 1s-Slater-type basis, meaning that we used four atomic orbitals obtained by centering a 1s-Slater-type orbital [Eq. (4)] about each of the four nuclei. This is known as a "minimal" basis set in that only the 1s orbital is occupied in the ground state of an isolated hydrogen atom. Williams,[11] Magnasco and Musso,[13] and Wilson and Goddard[16] have used this basis set in their full CI calculations on the H_4 system.

Rubinstein and Shavitt,[18] and Silver and Stevens[23] have used a $1s, 1s'$-Slater-type basis set. The use of two $1s$ orbitals (having different exponents) in this "double-zeta" basis appears to be simply a convenient device whereby minor improvements can be made over the minimal basis wave function, most importantly in the region between the atoms. Bender and Schaefer[22] have gone a step further by adding p orbitals, using a $1s, 1s', 2p_x, 2p_y, 2p_z$-Gaussian-type basis in their calculations. This $1s$ orbital is a "contracted" sum of three Gaussians, while the $1s'$ orbital is a single Gaussian. Amazingly enough, full CI calculations with Gaussian orbitals have proved quite successful. Among the advantages of their use is the easy evaluation of multicenter integrals, while a disadvantage is that generally a large enough basis must be used so as to at least crudely be capable of representing a Slater function. A discussion of the philosophy behind these various choices of basis sets is given in the book by Schaefer.[39] One fact should be borne in mind: the number of configurations involved increases dramatically with the size of basis chosen. A full CI calculation for the linear geometry, for example, involves 12, 176, and 2172 configurations, respectively, for the $1s$; $1s, 1s'$; and $1s, 1s', 2p_x, 2p_y, 2p_z$ basis sets.

"Self-consistent field"

The "self-consistent-field" (SCF) calculation, as referred to in the papers of interest to us in this review, is a particular version of the Hartree-Fock approach. One seeks to minimize the energy using a wave function of the form

$$\psi_{\text{SCF}} = \frac{1}{\sqrt{4!}} \sum_{P} (-1)^P P[\Phi_1(1)\Phi_1(2)\Phi_2(3) \times \Phi_2(4)\alpha(1)\beta(2)\alpha(3)\beta(4)] . \tag{8}$$

However, in contrast to the most general Hartree-Fock approach, the molecular orbitals Φ_1 and Φ_2 are restricted in this method to be linear combinations of whatever basis functions are being used. In the case of the minimal basis set, then

$$\Phi_1(\vec{r}) = C_{1a}\chi(|\vec{r}-\vec{R}_a|) + C_{1b}\chi(|\vec{r}-\vec{R}_b|) + C_{1c}\chi(|\vec{r}-\vec{R}_c|) + C_{1d}\chi(|\vec{r}-\vec{R}_d|) , \tag{9}$$

and the coefficients C would be the quantities to be determined. Actually, for such a small basis, geometric symmetry alone will often be sufficient to determine these coefficients. Bender and Schaefer[22] and Tapia and Bessis[19-21] have used $1s, 1s', 2p_x\, 2p_y, 2p_z$ and $1s, 1s', 1s'', 2p_x, 2p_y, 2p_z$-Gaussian bases in their SCF calculations.

Both the SCF and the Heitler-London (HL) wave functions are contained as special cases within the corresponding full CI wave function. They offer shorter computing time at the cost of less-accurate results. In general, the SCF wave function exhibits too little spatial correlation amongst the four electrons; the HL wave function, too much. The SCF wave function is best suited to geometries in which all four atoms are closely spaced; the HL wave function, when the atoms are far apart. In any case, for a given basis, the full CI calculation always yields lower upper-bounds on the ground-state energy than either the HL or SCF methods.

Other methods

The same full CI wave function may be arrived at from either the valence-bond point of view, in which ionic configurations are added to the covalent configurations, or from the molecular-orbital point of view, in which excited configurations are added to the SCF configuration. There are a number of limited CI calculations (i.e., not full) based on one or the other of these viewpoints. These methods include the "group function" approach of Magnasco, Musso, and McWeeny,[14] and the "GI" method of Wilson and Goddard.[16,17] The "SCF + CI" method, which we shall take to mean the SCF configuration plus all singly and doubly excited configurations, has proved to be very successful for at least the linear geometry.[22] Bender and Schaefer,[22] Tapia and Bessis,[21] Kochanski *et al.*,[24] and Ree and Bender[25] have used this approach.

III. SURVEY OF NUMERICAL RESULTS

This section reviews numerical results obtained for the ground-state energy of the H_4 system by the *ab initio* techniques described previously. We first make use of these results to give some indication of when the concept of interacting H_2 molecules is valid and where it breaks down. Then we specialize to the problem of the angular (viz., Fig. 1) and intermolecular separation dependence of the H_2-H_2 interaction energy. At this stage quantitative comparison of the various computational methods is made.

Interacting H_2 molecules

One may identify a particular pair of hydrogen atoms as constituting an H_2 molecule if, when considered as a function of the distance between these two atoms, the energy of the full H_4 system is near a local minimum. A system of four infinitely separated hydrogen atoms has an energy of −2.00 hartrees.[32] The energy may be lowered to −2.35 hartrees by grouping the atoms into two infinitely separated pairs, with the distance between atoms composing a given pair being 1.40 bohrs. The H_2 molecule binding energy, 0.17 hartree, accounts for this energy reduction.[40] The energy of the H_4 system increases when the two pairs of hydrogen atoms are pushed close together; i.e., there is a repulsive short-range interaction between the two H_2 molecules.

One would expect the concept of interacting H_2 molecules to remain valid down to separations for which the interaction energy approaches the binding energy in magnitude. This appears to be borne out by the calculations. In Fig. 2, we show the Silver and Stevens[23] results for the rectangular geometry. The abscissa specifies one side of the rectangle(R_2); the curves are labelled according to the other (R_1). It is evident that the lowest energies are obtained when one side is near 1.40 bohr (the equilibrium H_2 bond length), and the other side is large. Decreasing this larger side (the intermolecular distance) results in exponential-like increase as seen in the curve labelled $R_1 = 1.4$. The effect of intermolecular distance on the local potential well associated with the H_2 bond length can be seen in the dotted portion of the curves, where R_1 is to be taken now as the intermolecular distance; and R_2, the bond length. The calculations of Conroy and Malli,[33] in particular their Fig. 6, suggest that the obvious trend here does indeed result in an eventual loss of the barrier for $R_2 > 1.4$ bohrs as R_1 is further decreased below 1.8 bohrs. Somewhat before this point, the vibrational zero-point energy of the two molecules associated with the coordinate R_2 (about 0.02 hartree as estimated from the curvature at $R_2 = 1.4$ bohrs) will result in loss of the H_2 bonds.

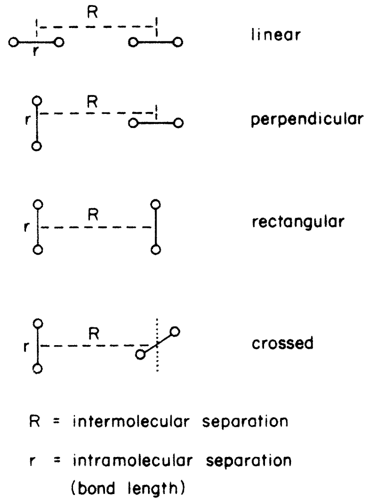

FIG. 1. Geometries of the H_4 system. The linear, perpendicular, and rectangular arrangements lie in the plane of the paper as shown. In the crossed geometry, the intramolecular axis of the right-hand molecule is perpendicular to the plane of the paper.

Does the optimal bond length change as the two molecules are pushed closer together? Analytic fits to the potential wells shown in Fig. 2 yield minima within a percent of 1.40 bohrs for the range of intermolecular separations from 2.8 to 1.8 bohrs. On the other hand, Conroy and Malli,[33] Wilson and Goddard,[17] and Tapia *et al.*[19,21] have reported results for the same rectangular geometry suggesting the optimal bond length shrinks as the intermolecular distance is decreased. From the first two of these papers, the shrinkage may be estimated to be about 4% for intermolecular separations near 2.2 bohrs. For two H_2 molecules approaching each other in a linear manner, the results of Wilson and Goddard,[16] as seen in their Fig. 18, suggest a similar shrinking of the optimal bond length. Extrapolation of their data suggests about a 4% effect for intermolecular separations near 3.1 bohrs. Recent work of Ree[41] implies the optimal bond length decreases for all geometries shown in Fig. 1. He obtains somewhat larger effects. The important point to bear in mind, as can be seen in Fig. 2, is that these uncertainties in the bond length lead to errors in

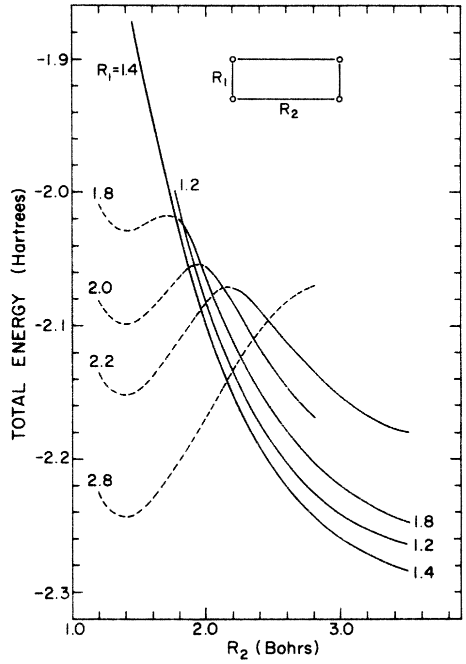

FIG. 2. Total energy of the H_4 system for the rectangular geometry. The abscissa specifies one side of the rectangle R_2 and the curves are labelled according to the length of the other side R_1. Both lengths are in bohrs. The H_2 bond length and the H_2-H_2 intermolecular separation may be identified with R_1 and R_2, respectively, for the solid curves; and the reverse, for the dashed curves. These results are from Silver and Stevens (Ref. 23).

the interaction energy generally less than a few percent. Accordingly, calculations of the H_2-H_2 interaction energy based on a fixed bond length of 1.40 bohrs should be valid to within this same accuracy.

As a rough summary one might say that the idea of the H_2 bond, and an associated length more or less equal to 1.4 bohrs, are relevant down to separations where the distance between the nearest atoms on two approaching molecules is about equal to, or perhaps half again as large, as this bond length. On further contraction, both the local potential wells signifying the bonds, and the associated length are lost. The Bender and Schaefer[22] results for the linear H_4 system, for example, show that in this regime it is energetically favorable to equally space the four atoms rather than trying to maintain the 1.4-bohr bond length (see Fig. 3). For lower (linear) densities this equally spaced geometry, while a bound state with respect to four separated atoms, is clearly unstable with respect to the formation of H_2 molecules.

Interaction energy

A partial judgement of the relative merit of the computational techniques can be made by checking their results for the ground-state energy of a single H_2 molecule (see Table I). Since these calculations are variational, the results are quite as expected: Lower energies are obtained by using larger basis sets, and by including all possible configurations (full CI) which may be constructed from the given basis set. This table is only indirectly related to our problem, however, since we are interested in *relative* changes in the energy of the H_4 system as the constituent H_2 molecules are moved about. The interaction energy of two H_2 molecules is calculated as the energy of the H_4 system less the energy of two infinitely separated molecules evaluated in the *same* approximation. Thus, for example, the large-basis SCF calculations of the interaction energy are superior to the minimal-basis full CI results, in spite of the fact that the latter technique gives the lower H_2 molecule ground-state energy.

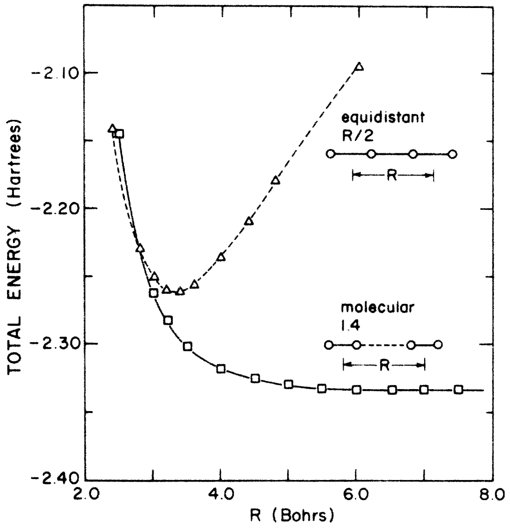

FIG. 3. Total energy of the H_4 system for the linear geometries. The solid curve corresponds to the "molecular" arrangement in which the atoms are grouped into two pairs, as shown, with a "bond length" of 1.4 bohrs. The dashed curve corresponds to the "atomic" arrangement in which the atoms are equally spaced, the interatomic separation being $R/2$. The curves intersect for $R = 2.8$ bohrs. These results are from Bender and Schaefer (Ref. 22).

The results of minimal-basis full CI calculations by Magnasco and Musso,[13] Williams,[11] and Wilson and Goddard[16] are shown in Fig. 4 for the linear and rectangular geometries. The density dependence is roughly exponential, $e^{-\alpha R}$, with α ranging between 1.80 and 1.85 bohrs^{-1} for the linear and 1.67–1.90 bohrs^{-1} for the rectangular geometry as the intermolecular distance R is increased from 3 to 5 bohrs. The Williams[11] results place the energy of the crossed and of the perpendicular geometries, respectively, about 15% below and 50% above those of the rectangular geometry. In contradiction to the statement made by Hoover *et al.*,[10] it is clear that the interaction energy of the linear geometry as calculated with the minimal basis set is only about a factor of 2 larger than that of the rectangular geometry. We have also included in Fig. 4 the results of the Heitler-London calculation using correct multicenter integrals.[44] The fairly close agreement with the full CI results clearly points out the danger of using approximate multicenter integrals as in the early Heitler-London calculations by de Boer,[36] and Mason and Hirschfelder.[38] An angular dependence more than twice as large as seen here was reported in those papers.

The results of CI calculations using larger bases (specified in Table I) are shown in Figs. 5 and 6.[45] The results of Bender and Schaefer[22] and of Silver and Stevens[23] shown here are from full CI calculations. Those of Tapia and Bessis[21] and of Kockanski *et al.*[24] are from the SCF + CI technique, which gives values for the interaction energy within a few percent of full CI values for the linear case.[22] For intermolecular separations R around 3 bohrs, the curves in Fig. 5 have about the same dependence on this parameter as in the minimal-basis calculations, i.e., $e^{-\alpha R}$ with $\alpha = 1.81$ and 1.62 bohrs^{-1} for the linear and rectangular cases, respectively. The actual values of the interaction

TABLE I. Ground-state energy of the H_2 molecule as calculated in various approximations.

Basis	Type	Exponent	r_0[a]	Reference	HL[b]	SCF[b]	SCF+CI[b]	Full CI[b]
1s	Slater	1.193	1.4166	Magnasco and Musso[13] Williams[11]	−1.138 20[c]	−1.127 98		−1.147 89
		1.05	1.4	Wilson and Goddard[16]		−1.128 19		−1.147 91[d]
1s, 1s'	Slater	0.9, 1.2	1.4	Silver and Stevens[23]				−1.151 75
1s, 1s', 1s'', $2p_x$, $2p_y$, $2p_z$[e]	Gaussian		1.4166	Tapia and Bessis[21]		−1.125 50	−1.135 10	
1s, 1s', $2p_x$, $2p_y$, $2p_z$[f]	Gaussian		1.4	Bender and Schaefer[22] Ree and Bender[25]		−1.131 20	−1.165 19	−1.165 70
1s, 1s', 1s'', $2p_x$, $2p_y$, $2p_z$, $2p_x'$, $2p_y'$, $2p_z'$[g]	Gaussian		1.4	Kochanski *et al.*[24]			−1.168 02	−1.168 60
James-Coolidge function	100 terms		1.4	Kolos and Roothaan[42] Kolos and Wolniewicz[40]		−1.133 64		−1.174 47
Experiment				Stoicheff[43]				−1.174 45

[a] Bond length in bohrs, 1 bohr = 0.529 17 Å.

[b] Energy in hartrees, 1 hartree = 27.211 eV.

[c] Evaluated for this choice of parameters by the authors.

[d] $r_0 = 1.4166$.

[e] Each function is a single Gaussian.

[f] The 1s function is a contracted sum of three Gaussians.

[g] The 1s function is a contracted sum of four Gaussians.

energy, however, are smaller by 36% and 12% respectively. This reduces the rectangular-to-linear variation from about a factor of 2.2 to 1.6. In Fig. 6 it is seen that the interaction energy of the perpendicular geometry has also been reduced relatively more strongly than that of the rectangular case, so that only about a 15% variation in energy is involved in changing the orientation from the crossed to the rectangular, and then to the perpendicular geometry.

For values of the intermolecular separation greater than about 4 bohrs, Fig. 5 shows that the interaction energy begins to fall off considerably faster than an exponential. This behavior, which was only barely suggested by the minimal-basis calculations, reflects the importance of the attractive van der Waals or dispersion forces in this region. In fact, Tapia and Bessis,[21] Bender

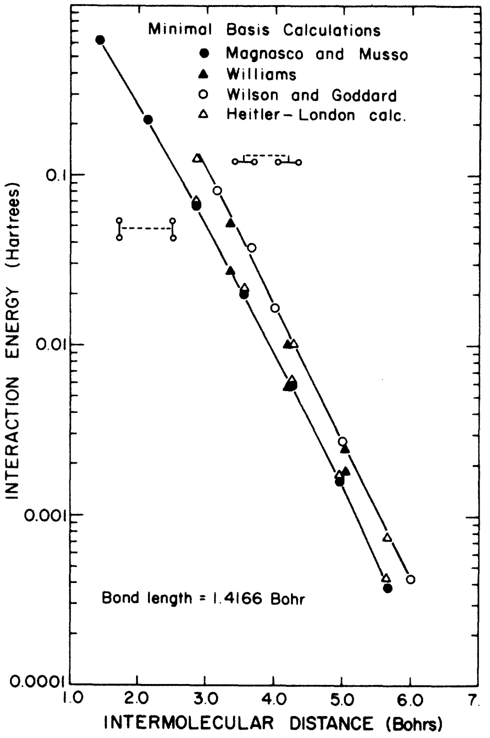

FIG. 4. Minimal-basis calculations of the H_2-H_2 interaction energy for linear and rectangular geometries. The full CI results of Magnasco and Musso (Ref. 13), Williams (Ref. 11), and Wilson and Goddard (Ref. 16) are shown. Results of the Heitler-London calculations (Ref. 44) are included for comparison. The two curves differ by a factor of 2.2, 1.9, and 1.8 for intermolecular separations of 3, 4, and 5 bohrs, respectively. The uppermost two points of Wilson and Goddard were obtained with a bond length of 1.4 bohrs. The lowest two points of Magnasco and Musso are from their limited CI calculations (Ref. 12). Some of Williams' questionable (Ref. 12) large separation results have been omitted.

and Schaefer,[22] and Kochanski *et al.*[24] have all observed some form of attractive van der Waals minimum (depth ~ 10^{-4} hartree) in the interaction energy for intermolecular separations around 6.5–7.0 bohrs. Kochanski *et al.* note that calculations in this region are extremely sensitive to the choice of basis, and that a $2p$ orbital with a small exponent is essential. In contrast to the orientation dependence seen for smaller separations, Kochanski *et al.* find the perpendicular geometry to be most stable for intermolecular separations greater than about 4.5 bohrs. There does not appear to be any one type of force responsible for this fact, as they note that the valence, quadrupole, and the dispersion forces all contribute to this stability.

Margenau and Kestner[46] have argued that an SCF calculation of the interaction energy cannot include dispersion effects. This seems intuitively clear in that electron-electron correlations (aside from those originating from the antisymmetrization) are not incorporated in the SCF wave function, and such correlations would appear to be essential to an induced dipole-induced dipole interaction. In Fig. 7 we show the results of SCF calculations by Bender and Schaefer[22] and by Tapia and Bessis[21] which are consistent with these expectations. For intermolecular separations less than 3 bohrs, these results are in fairly close agreement with the CI calculations. For larger separations they fall off too slowly, roughly exponentially, and do not display an attractive van der Waals minimum. For very large separations, greater than 12.5 bohrs, the SCF calculations of Bender, Schaefer, and Kollman[47] are in quantitative agreement with the predicted classical quadrupole-quadrupole interaction.

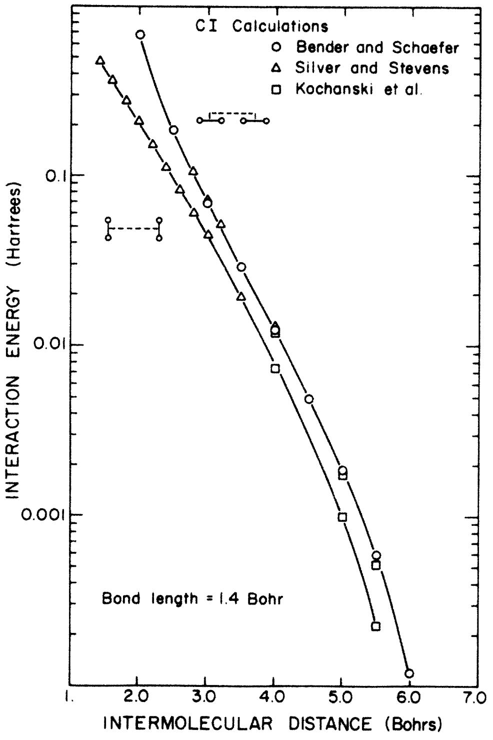

FIG. 5. Extended-basis calculations of the H_2-H_2 interaction energy for linear and rectangular geometries. The results of Bender and Schaefer (Ref. 22) and of Silver and Stevens (Ref. 23) are full CI, while those of Kochanski *et al.* (Ref. 24) were obtained by the SCF + CI technique. The bases used are specified in Table I. The two curves differ by a factor of 1.6, 1.6, and 1.9 for intermolecular separations of 3, 4, and 5 bohrs. For these same separations, the linear results are lower by 36%, 27%, and 31%, respectively, in comparison to the corresponding minimal-basis results (Fig. 4); while the rectangular results are lower by 12%, 12%, and 34%, respectively, in comparison to the rectangular results in Fig. 4.

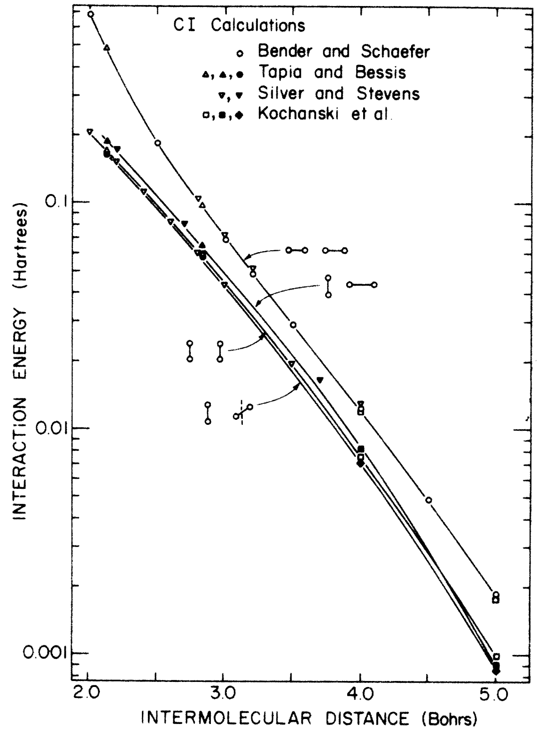

FIG. 6. Extended-basis calculations of the H_2-H_2 interaction energy for various geometries. The results of Bender and Schaefer (Ref. 22) and of Silver and Stevens (Ref. 23) are full CI, while those of Tapia and Bessis (Ref. 21) and of Kochanski *et al.* (Ref. 24) were obtained by the SCF + CI technique. The bases used are specified in Table I. The results for the linear and rectangular geometries (open symbols) are identical to those in Fig. 5. For intermolecular separations from 3 to 4 bohrs, the results for the perpendicular and crossed geometries (closed symbols) are, respectively, about 10% above and 5% below those for the rectangular geometry.

To summarize this section, we note that CI calculations using an extended basis that includes a diffuse $2p$ orbital appear to be necessary to accurately determine the H_2-H_2 interaction energy for all separations. There is sufficient numerical agreement for intermolecular separations between 2 and 5 bohrs to suggest that the curves in Figs. 5 and 6 are correct to within better than 10%. Furthermore, these results are expected to include *all* contributions to the interaction energy.

IV. ANALYTIC EXPRESSIONS

The interaction energy of two hydrogen molecules is generally subdivided into contributions from (i) the short-range valence (overlap, or exchange) forces, (ii) the long-range dispersion forces, and (iii) the electrostatic quadrupole-quadrupole forces. Analytic expressions for the latter two contributions are fairly well established.[34, 48–50] We confine our attention to the short-range part of the interaction energy.

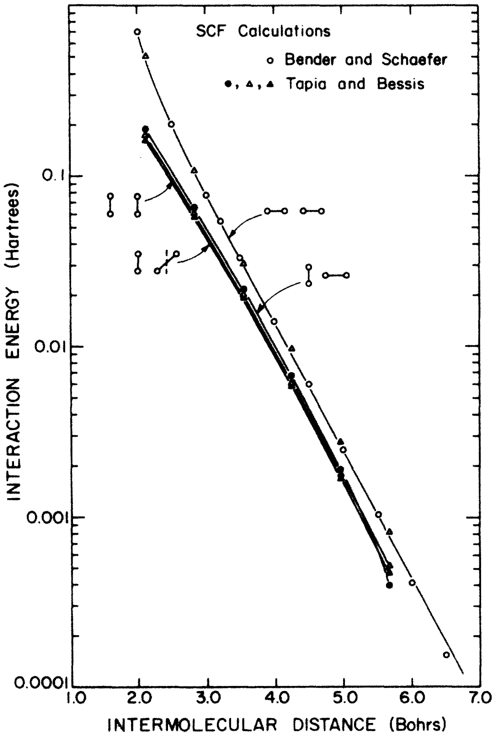

FIG. 7. Extended-basis SCF calculations of the H_2-H_2 interaction energy for various geometries. The SCF results of Bender and Schaefer (Ref. 22) and Tapia and Bessis (Ref. 21) are shown. The choice of basis is specified in Table I. For intermolecular separations less than about 3.0 bohrs these results are generally within a few percent agreement with the CI results shown in Figs. 5 and 6. For intermolecular separations around 5 bohrs, these SCF results are higher than the CI results by about (35–90%), depending on geometry.

Both de Boer[36] and Abrikosov[2] chose forms for the valence contribution which may be interpreted as representing pairwise interactions between the *atoms* making up the two H_2 molecules:

$$\Phi^{(\mathrm{val})} = \epsilon(R_{ac}) + \epsilon(R_{ad}) + \epsilon(R_{bc}) + \epsilon(R_{bd}) \, . \qquad (10)$$

Atoms a and b constitute one molecule; c and d, the other. While de Boer chose an exponential for the function $\epsilon(R)$, Abrikosov used an appropriate average of the singlet and triplet interactions between two hydrogen atoms. In light of the results discussed in Sec. III, however, there are serious objections to the general form given by Eq. (10). If the intramolecular separation is taken to be near 1.4 bohrs, any choice for the function $\epsilon(R)$ giving the right dependence on intermolecular separation for some particular geometry results in an orientation dependence of about a factor of 5. Yet all *ab initio* calculations have shown an overall orientation dependence of a factor of 2 or less. It is to be emphasized in particular, that the de Boer potential can *not* adequately represent any of the results discussed in Sec. III, including the minimal basis work. Neece *et al.*[8] were able to fit the Magnasco and Musso[13] results with a de Boer potential only because the Magnasco and Musso work did not include any of the high-energy geometries such as the perpendicular or linear arrangements. These facts are illustrated in Fig. 8, where the de Boer potential with the choice of parameters used by Neece *et al.*, is plotted for the standard geometries, and compared to minimal-basis full CI calculations for the rectangular and linear cases.

Equation (10) can be made to yield an overall dependence on orientation of about a factor of 2 if the intramolecular separation is artificially chosen to be a third or so smaller than 1.4 bohrs. However, in this case the perpendicular geometry still falls midway between the linear and rectangular results, and the dependence of the interaction energy on intermolecular separation can not be made satisfactory for all geometries.

The close agreement of the Heitler-London calculations with the minimal-basis full CI results shown in Fig. 4, might suggest that de Boer's original goal of selecting out a few dominant terms from the Heitler-London expression might still be achieved. Unfortunately, there are simply too many equally large, and partially cancelling terms for this to be feasible. The angular dependence immediately suffers from such selection processes. For example, in their book Margenau and Kestner[34] make a slight approximation in the Heitler-London expression based on neglecting the fourth power of the ratio of the inter- to intramolecular overlap integrals. Evaluation of this expression using correct multicenter integrals yields results about 20% higher for the rectangular geometry and about 100% higher for the linear geometry, in comparison with the full Heitler-London result.

The angular dependence of the interaction potential appears to be of rather high order, as is evidenced in Fig. 6. Low-order terms of the form

$$(\cos^2\theta_1 + \cos^2\theta_2) f(R),$$

where θ_1 is the angle between the axis of the first molecule and the line joining the centers of mass of the two molecules, would place the perpendicular results halfway between those for the rectangular and linear cases. This is clearly not the case.

The problem of fitting the angular behavior may be avoided in first approximation by performing some form of average over the angular variables, as is done by Hoover *et al.*[10] and by Ree and Bender.[25] Hoover *et al.* arrive at the potential

$$\Phi = \frac{8.2e^2}{a_0}\, e^{-1.74x} - \frac{e^2}{a_0}(13x^{-6} + 116x^{-8}) e^{-400x^{-6}}, \tag{11}$$

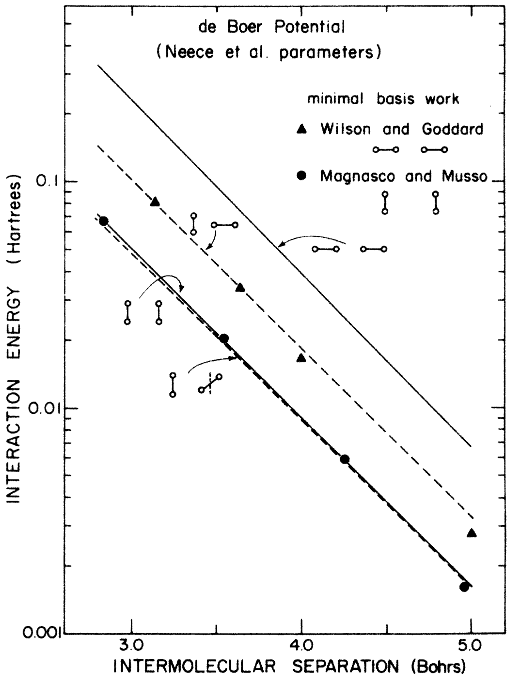

FIG. 8. de Boer potential for various geometries. The de Boer potential is plotted for the choice of parameters used by Neece *et al*. (Ref. 8), i.e., $\epsilon(R) = 3.2e^{-1.7639R}$ [atomic units, see Eq. (10)]. While the curve for the rectangular case is in close agreement with the calculations of Magnasco and Musso (Ref. 13), the curve for the linear case is too high by about a factor of 2 in comparison to the calculations of Wilson and Goddard (Ref.16).

where $x = R/a_0$ and $a_0 = 1$ bohr $= 0.52917$ Å. The first term is the valence energy, which they obtain by a spherical average over SCF calculations for the four standard geometries. The second term is the usual expression for the dispersion energy,[49, 50] multiplied by a short-range cutoff factor as suggested by Trubitsyn.[5] From a similar spherical average of their SCF + CI calculations for the four geometries, Ree and Bender obtain

$$\Phi = (3.536e^2/a_0)\, e^{-1.242x - 0.06784x^2}, \tag{12}$$

for $2.5 < R < 4.5$ bohrs. As noted earlier, this expression should already include dispersion effects. A spherical average of the results illustrated in Fig. 6 may be fit by

$$\Phi = (2.184e^2/a_0) e^{-0.8431x - 0.13811x^2}, \tag{13}$$

which agrees to within 10% of the Ree and Bender expression throughout the range 3–4.5 bohrs. The Evett and Margenau[37] averaging procedure yields results only a few percent different from that of Hoover *et al.*,[10] which we have used in arriving at Eq. (13).

The various potentials [Eqs. (11)–(13)] are shown in Fig. 9. On purely formal grounds, the extended-basis CI results [solid curves, Eqs.(12) and (13)] must be considered the most reliable determinations of the spherically averaged interaction between two hydrogen molecules. They represent agreement to within about 10% of most of the recent *ab initio* CI calculations, and incorporate the dispersion effects in a fundamental manner. In contrast, the expression of Hoover *et al.* [dashed line, Eq. (11)] relies on the presumption that the standard long-range expression for the dispersion energy may also be applied for short intermolecular separations. It is in fact this contribution which is responsible for the significantly weaker repulsion of Eq. (11) as compared to Eqs. (12) and (13). We also show in Fig. 9 the potential used by Neece *et al.*,[8] which consists of a de Boer form for the valence contribution plus the Margenau[49] result for the dispersion energy. Since their calculation of the energy of the molecular solid was based on the "α-nitrogen" structure, we have plotted their potential (dotted curve) for the near-neighbor molecular orientations of this structure. This geometry is close in energy to the perpendicular case, and so the de Boer potential has significantly overestimated the repulsive energy.

In spite of the consistency evidenced amongst the recent extended-basis CI calculations for the H_2-H_2 interaction potential, there is not good agreement between theory and experiment. The shaded region in Fig. 9 represents the determination by Hoover *et al.*[10] of bounds on an effective pair potential which would be consistent with the shock experiments of Dick[28] and van Thiel *et al.*[27,29] More recently, van Thiel *et al.*[31] have reported shock experiments on deuterium which are in excellent agreement with an analysis based on Eq. (11) (dashed curve in Fig. 9). Experimental determinations of the pair potential are evidently a factor of 2 or so smaller than the *ab initio* theoretical calculations. The recent work of Ree and Bender[25] suggests that this discrepancy is due to the breakdown of pairwise additivity for short-range interactions amongst hydrogen molecules in the bulk.

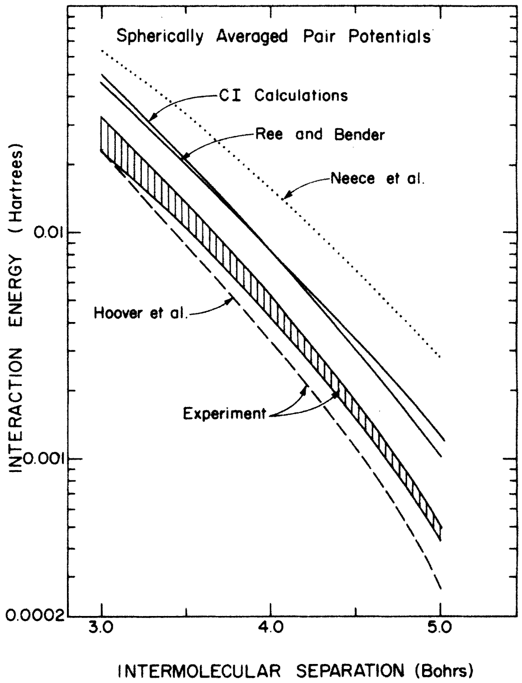

FIG. 9. Spherically averaged H_2–H_2 interaction potential. The solid curves labelled "CI calculations" and "Ree and Bender" are from *ab initio* calculations, and are plots of Eqs. (13) and (12), respectively. The shaded region labelled "Experiment" corresponds to the determination by Hoover *et al.* (Ref. 10) of bounds on an effective pair potential consistent with shock experiment (Ref. 29). More recent shock experiments (Ref. 31) are consistent with analyses based on the dashed curve, which is a plot of Eq. (11), the potential determined by Hoover *et al.* The dotted curve is a plot of the potential used by Neece *et al.* (Ref. 8) for the molecular orientations characteristic of near neighbors in the α-nitrogen structure. Calculations of the $T=0$ molecular-to-atomic phase transition pressure by Neece *et al.* (using the dotted curve), Hoover *et al.* (using the upper bound to the shaded region), and by van Thiel *et al.* (Ref. 31) (using the dashed curve) yield 0.84, 1.7, and 4.2 Mbar, respectively. In each case the atomic calculations of Neece *et al.* were used.

V. APPLICABILITY TO THE SOLID

The assumption of pairwise additivity means that the behavior of a system of many molecules is characterized by a many-body potential of the form

$$V=\sum_{i<j}\Phi_{ij} , \tag{14}$$

where Φ_{ij} is the interaction potential for an *isolated* system of two molecules. The calculations of Ree and Bender,[25] unfortunately, point to rather large non-pairwise-additive contributions to the interaction energy of a collection of H_2 molecules for intermolecular separations less than 4.5 bohrs. A many-body potential of the form given by Eq. (14) may still be adequate, but then one must replace Φ_{ij} by some *effective* pair potential Φ_{ij}^{eff}. Ree and Bender suggest on the basis of their calculations for a system of three H_2 molecules that triplet corrections to the "bare" pair potential Φ_{ij} may be adequate to give a Φ_{ij}^{eff} in fair agreement with the phenomenological potentials for intermolecular separations down to about 3.5 bohrs.

With an eye towards calculation of the properties of the solid, the unfortunate aspect of these results is that a rigorous theoretical determination of the short-range part of the pair potential appropriate to a solid is still to be accomplished, and is now considerably more complex. It does not appear that one can avoid performing *ab initio* calculations for three and perhaps more molecules. For example, one might have expected that imposition of appropriate symmetry constraints on an H_4 calculation might improve matters. As an illustration, CI calculations for the linear H_4 system permit an imbalance in the weighting of ionic configurations for the inner with respect to the outer atoms. In a solid with inversion symmetry, these must have equal weight. However, agreement of the Heitler-London results with the minimal-basis full CI results for this geometry suggests that at least in this case the matter of symmetry is not important.

A comment should be made on the applicability of the spherically averaged potential to calculations for the solid. Because of the small molecular moment of inertia and the weak angular forces, it is well known that at atmospheric pressure, the H_2 molecules in solid hydrogen are essentially freely rotating.[51] As the solid is compressed, however, the size of the anisotropic component of the interaction energy continues to increase, until eventually the molecules undergo rotational oscillations about some preferred orientations. Since the low-lying eigenfunctions of a free rotator are sizeable throughout much of the angular phase space, in contrast to the more localized eigenfunctions of a rotational oscillator, a spherical average over the angular variables of the interaction potential is expected to be a good approximation in this limit. A rough criterion for rotational behavior would be to require that the barrier to rotation U_0 be considerably smaller than, say, the $J=1\rightarrow 3$ (orthohydrogen) level spacing of the free rotator,

$$U_0 < 10\hbar^2/2I = 0.003 \text{ hartree },$$

where J and I are, respectively, the angular momentum and moment of inertia of an H_2 molecule. The overall angular variation of the interaction potential as seen in Fig. 6 is already of this order for intermolecular separations of about 5 bohrs. Detailed calculations by Raich and Etters[51] place the transition from rotation to rotational oscillation at densities corresponding to a near-neighbor separation of about 4.7 bohrs. These results are based on the exaggerated angular dependence of the de Boer potential, and so it is likely that rotational behavior persists for near-neighbor separations smaller than this. The molecular phase is likely to be stable for intermolecular separations as small as 3.5 bohrs,[10] and so the spherical average is probably not always an adequate approximation for *ground-state* energy calculations. Ebner and Sung,[52] in particular, have stressed the importance of retaining the anisotropic interaction in such calculations. It is felt that the spherical average is justified for the high temperatures involved in the shock experiments.[10]

As mentioned in the Introduction, one source of interest in the short-range part of the H_2-H_2 interaction potential is the desire to accurately determine the molecular-to-atomic phase-transition pressure. Qualitative aspects of this problem are evident in even the simple linear versus equidistant H_4 systems, whose energies are plotted in Fig. 3. In this figure, one can identify a zero-pressure atomic phase (interatomic distance $R/2=1.7$ bohrs) that is unstable with respect to the corresponding zero-pressure molecular phase (intermolecular separation $R=6.5$ bohrs; the van der Waals minimum is not visible on this scale). At sufficiently high pressure, the atomic phase becomes the more stable. A common tangent construction even yields a reasonable transition pressure,

$$P=\Delta E/3R^2\Delta R = 3.3\times 10^{-3}\text{a.u} \simeq 1 \text{ Mbar},$$

where E is the energy per molecule and R is the intermolecular separation. Turning to serious calculations, we note that Neece *et al.*,[8] Hoover *et al.*,[10] and van Thiel *et al.*[31] have all used the *same* atomic phase calculations[8] in their determination of the transition pressure. A glance at the corresponding choices for the H_2-H_2 interaction potential thus offers an idea as to the sensitivity of the transition pressure to this choice. The molecular pair potentials used are (see Fig. 9) the dotted curve, the upper bound to the shaded region, and the dashed curve, respectively. The corresponding transition pressures are 0.84, 1.7, and 4.2 Mbar respectively. Trubitsyn[5] obtained a transition pressure of 4.6 Mbar using a molecular pair potential within 20% agreement of Eq. (11) (the dashed curve, Fig. 9) over the range 3–8 bohrs. If the non-pairwise-additive effects are indeed as large as suggested by Ree and Bender, then there is moderate agreement between theory and experiment, pointing to a transition pressure in the neighborhood of 4 Mbar, or larger.[31]

VI. SUMMARY

Extended-basis CI calculations which include a diffuse $2p$ orbital appear to be capable of determining the total interaction energy between two hydrogen molecules for any separation. Consistent results among a number of such *ab initio* calculations suggests that the potential is known to better than 10% for intermolecular separations ranging from 2.5–5 bohrs. For slightly smaller separations, the composite H_2 bonds are likely to become unstable. The angular variation of the interaction potential in the above range is about 15%, except for geometries approaching the linear arrangement, in which case the potential may increase by about 60%. There are not yet sufficient data to determine the analytic form of this dependence, although it appears to be of relatively high order. Analytic forms for a spherical average over the angular degrees of freedom are readily obtained. As a function of intermolecular separation, such potentials fall off somewhat faster than an exponential.

With respect to a pair potential suitable for use in highly compressed liquid or solid molecular hydrogen, the situation is somewhat more complex. It appears that three-body corrections must be added to the bare pair potential for intermolecular separations between 3.5 and 4.5 bohrs, and that at shorter separations even higher many-body corrections may be necessary. Such corrections lead to much improved agreement between the *ab initio* calculations and analyses of shock experiments, with the implication that the $T=0$ molecular-to-atomic phase transition in solid hydrogen occurs in the neighborhood of 4 Mbar.

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[44] We have evaluated the Heitler-London expression for the rectangular and linear geometries, taking $\zeta=1.193$ and $r_0=1.4166$ bohrs. For the rectangle, the exact multicenter integrals tabulated by Magnasco and Musso (Refs. 12 and 13) were used. In the linear case, the integrals were evaluated using a six Gaussian expansion of the Slater function [S. Huzinaga, J. Chem. Phys. 42, 1293 (1965)]. This procedure was tested for the rectangular case. The resultant values of the interac-

tion energy were accurate to better than ± 0.0001 hartree.

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