

The Energy of the Hydrogen Molecule

E. F. Gurnee and J. L. Magee

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II. Calculations of Energy for Normal H₂ Molecule

For computational purposes, it is convenient to rearrange the wave function for the normal hydrogen molecule into the form:

$$\Psi_{WIP} = \Psi_o + \alpha\Psi_s + \beta\Psi_c + \gamma\Psi_p,$$

where:

$$\begin{aligned}\Psi_o &= a_o(1)b_o(2) + a_o(2)b_o(1) \\ \Psi_s &= [a_s(1)b_s(2) + a_s(2)b_s(1)] \cos(\phi_2 - \phi_1) \\ \Psi_c &= a_c(1)b_c(2) + a_c(2)b_c(1) \\ \Psi_p &= a_o(1)a_o(2) + b_o(1)b_o(2).\end{aligned}$$

Then, since the Hamiltonian can be written:

$$H = -(1/2)\Delta_1 - (1/2)\Delta_2 - r_{a1}^{-1} - r_{a2}^{-1} - r_{b1}^{-1} - r_{b2}^{-1} + r_{12}^{-1} + R^{-1}.$$

It is easy to show that:

$$\begin{aligned}H\Psi_o &= (-z^2 + R^{-1})\Psi_o + a_o(1)b_o(2) \\ &\quad \times [(z-1)(r_{a1}^{-1} + r_{b2}^{-1}) - r_{a2}^{-1} - r_{b1}^{-1} + r_{12}^{-1}] \\ &\quad + a_o(2)b_o(1)[(z-1)(r_{a2}^{-1} + r_{b1}^{-1}) - r_{a1}^{-1} - r_{b2}^{-1} + r_{12}^{-1}]\end{aligned}$$

$$\begin{aligned}H\Psi_s &= (-z^2 + R^{-1})\Psi_s + a_s(1)b_s(2) \cos(\phi_2 - \phi_1) \\ &\quad \times [(2z-1)(r_{a1}^{-1} + r_{b2}^{-1}) - r_{a2}^{-1} - r_{b1}^{-1} + r_{12}^{-1}] + a_s(2)b_s(1) \\ &\quad \times \cos(\phi_2 - \phi_1)[(2z-1)(r_{a2}^{-1} + r_{b1}^{-1}) - r_{a1}^{-1} - r_{b2}^{-1} + r_{12}^{-1}]\end{aligned}$$

$$\begin{aligned}H\Psi_c &= (-z^2 + R^{-1})\Psi_c + a_c(1)b_c(2) \\ &\quad \times [(2z-1)(r_{a1}^{-1} + r_{b2}^{-1}) - r_{a2}^{-1} - r_{b1}^{-1} + r_{12}^{-1}] \\ &\quad + a_c(2)b_c(1)[(2z-1)(r_{a2}^{-1} + r_{b1}^{-1}) - r_{a1}^{-1} - r_{b2}^{-1} + r_{12}^{-1}]\end{aligned}$$

$$\begin{aligned}H\Psi_p &= (-z^2 + R^{-1})\Psi_p + a_o(1)a_o(2) \\ &\quad \times [(z-1)(r_{a1}^{-1} + r_{a2}^{-1}) - r_{b1}^{-1} - r_{b2}^{-1} + r_{12}^{-1}] \\ &\quad + b_o(1)b_o(2)[(z-1)(r_{b1}^{-1} + r_{b2}^{-1}) - r_{a1}^{-1} - r_{a2}^{-1} + r_{12}^{-1}].\end{aligned}$$

Thus it follows that the approximate energy is given as the lowest root of the secular equation:

$$|zU_{ij} + z(z-1)C_{ij} - (E + z^2 - zq^{-1})N_{ij}| = 0.$$

Here:

$U_{oo} = B_o + D_o$	$C_{oo} = 2 + Q_o$	$N_{oo} = 1 + S_o$
$U_{ss} = B_1 + D_1$	$C_{ss} = 4 + Q_1$	$N_{ss} = 2 + S_1$
$U_{cc} = B_2 + D_2$	$C_{cc} = 2 + Q_2$	$N_{cc} = 1 + S_2$
$U_{pp} = B_6$	$C_{pp} = 2 + Q_6$	$N_{pp} = 1 + S_o$
$U_{os} = (B_3 + D_3)/2$	$C_{os} = 0$	$N_{os} = 0$
$U_{oc} = (B_4 + D_4)/2$	$C_{oc} = Q_4/2$	$N_{oc} = -S_3/2$
$U_{op} = B_9/2$	$C_{op} = Q_9/2$	$N_{op} = S_9/2$
$U_{sc} = (B_5 + D_5)/2$	$C_{sc} = 0$	$N_{sc} = 0$
$U_{sp} = B_7/2$	$C_{sp} = 0$	$N_{sp} = 0$
$U_{cp} = B_8/2$	$C_{cp} = 0$	$N_{cp} = 0$

where:

$zB_o = -2G_o + K_{oo,oo}$	$zD_o = -2J_o I_{oo} + L_{oo,oo}$	$S_o = (I_{oo})^2$
$zB_1 = -2G_s + K_{ss,ss} + 2z$	$zD_1 = L_{ss,ss}$	$S_1 = I_{ss}$
$zB_2 = -2G_c + K_{cc,cc} + z$	$zD_2 = L_{cc,cc}$	$S_2 = (I_{cc})^2$
$zB_3 = 2K_{os,os}$	$zD_3 = 2L_{os,os}$	$S_3 = (I_{co})^2$
$zB_4 = 2K_{oc,oc}$	$zD_4 = 2L_{oc,oc} + 4I_{co}J_{co}$	$S_4 = 4I_{oo}$
$zB_5 = 2K_{cs,cs}$	$zD_5 = 2L_{cs,cs}$	$zQ_o = 2I_{oo}J_o$
$zB_6 = -2G_o + (5/8)z - 2I_{oo}J_o + L_{oo,oo}$		$zQ_1 = 4J_s$
$zB_7 = 4L(a_o, a_s; a_o, b_s)$		$zQ_2 = 4I_{cc}J_c$
$zB_8 = 4I_{co}G_{co} + 4L(a_o, a_c; a_o, b_c)$		$zQ_3 = -8I_{co}J_{co}$
$zB_9 = -4I_{oo}G_o - 4J_o + 4L(a_o, a_o; a_o, b_o)$		$zQ_4 = 2I_{oo}J_{oo}$
		$zQ_5 = 4J_o + 4I_{ooo}$

The best value of z to use in the secular equation is determined from the condition: $Z = -q(\partial E/\partial q)_z/(\partial E/\partial Z)_q$. Thus, at each value of q , the energy is calculated from the secular equation for each of a number of values of z from which the value of $(\partial E/\partial Z)_q$ can be estimated. Then comparing values of E calculated for the same value of z but for different values of q , we obtained estimates of $(\partial E/\partial q)_z$. An analytical curve fitting method was developed to simplify the work indicated above.

III. Calculations of Energy for First Excited State of H₂ Molecule

The wave function for the first excited ($^3\Sigma$) state of the hydrogen molecule can be written in the form:

$$\Psi_{WP} = \Psi_o' + \alpha\Psi_s' + \beta\Psi_c',$$

where:

$$\begin{aligned}\Psi_o' &= a_o(1)b_o(2) - a_o(2)b_o(1) \\ \Psi_s' &= [a_s(1)b_s(2) - a_s(2)b_s(1)] \cos(\phi_2 - \phi_1) \\ \Psi_c' &= a_c(1)b_c(2) - a_c(2)b_c(1).\end{aligned}$$

The approximate energy is then given as the lowest root of the secular equation:

$$|zU_{ij}' + z(z-1)C_{ij}' - (E + z^2 - zq^{-1})N_{ij}'| = 0.$$

Here:

$U_{oo}' = B_o - D_o$	$C_{oo}' = 2 - Q_o$	$N_{oo}' = 1 - S_o$
$U_{ss}' = B_1 - D_1$	$C_{ss}' = 4 - Q_1$	$N_{ss}' = 2 - S_1$
$U_{cc}' = B_2 - D_2$	$C_{cc}' = 2 - Q_2$	$N_{cc}' = 1 - S_2$
$U_{os}' = (B_3 - D_3)/2$	$C_{os}' = 0$	$N_{os}' = 0$
$U_{oc}' = (B_4 - D_4)/2$	$C_{oc}' = Q_4/2$	$N_{oc}' = S_3/2$
$U_{op}' = (B_5 - D_5)/2$	$C_{op}' = 0$	$N_{op}' = 0$

Here the B_i , D_i , Q_i , and S_i have the same meaning as in the case of the normal H₂ molecule.

The Energy of the Hydrogen Molecule

E. F. GURNEE AND J. L. MAGEE

Radiation Chemistry Project, Department of Chemistry, University of Notre Dame,¹ Notre Dame, Indiana

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A simple two-parameter variational function has been used to calculate the energy of normal H₂. The first parameter is the usual scale factor; the second parameter is a distance of displacement of the atomic orbitals (see Fig. 1). The best potential energy is obtained as approximately 96 kcal per mole for internuclear separation 1.45 a₀. The behavior of the new parameter as a function of internuclear separation is discussed.

A RECENT reinvestigation of the interaction of two hydrogen atoms by Hirschfelder and Linnett² has suggested that trial wave functions for H₂ may be improved by allowing the electrons to spend more time

in the region between the nuclei. This idea has been tested with the simplest wave function for H₂ (the Heitler-London wave function) by shifting the atomic orbital centers closer together than the nuclei (see Fig. 1). The distance in Bohr radii that each center is shifted, x , is used as a variational parameter. It is easy to vary a scale factor z , so this has also been done.

¹ Supported by the AEC under contract number AT(11-1)-38.

² J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.* **18**, 130 (1950).

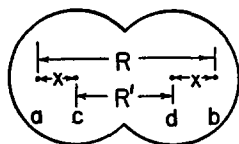


FIG. 1. The two nuclei are at a and b . The $1s$ orbitals have their centers at c and d .

TABLE I. Calculated values of the binding energy in Kcals./mole and the parameters x and z .

R	x	z	B.E.
1.00	0.06	1.275	59.6
1.20	0.03	1.23	85.3
1.40	0.06	1.185	94.7
1.50	0.08	1.16	95.1
1.60	0.10	1.13	92.2
1.80	0.130	1.07	82.2
2.00	0.115	1.03	67.8
2.41	-0.0158	1.0227	49.2
3.00	-0.0140	0.9925	26.3
4.05	-0.0048	0.9844	6.90
5.08	-0.0012	0.9932	1.49

The two-parameter wave function which we have used is thus:

$$\Psi = (z^3/\pi)^{1/2} [\exp(-zr_{c1} - zr_{d2}) + \exp(-zr_{c2} - zr_{d1})].$$

Here r_{c1} is the distance in Bohr radii of the first electron from the orbital center c (which is not the position of a nucleus), etc.

Calculation of the energy involves only standard techniques and will not be discussed here. There is, however, a three-center integral in the energy expression which does not usually occur in diatomic problems.

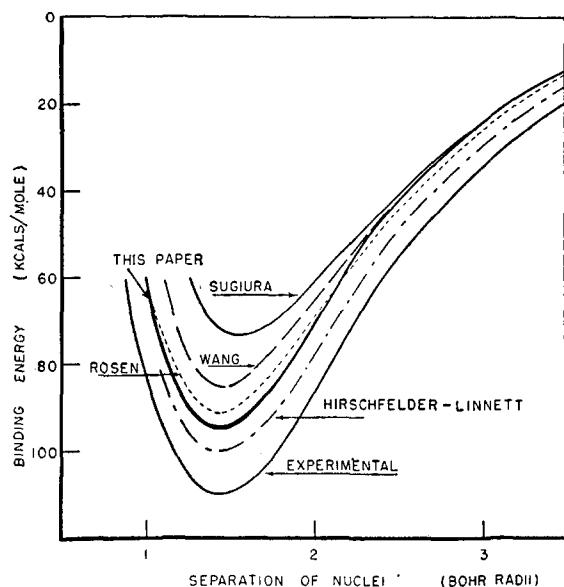


FIG. 2. Comparison of the energies of H_2 from several different calculations. At large distances the energy obtained in this work is always slightly lower than the Wang energy, which is slightly lower than the Sugiura energy, although the three are approximately equal.

TABLE II. Summary of H_2 calculations.

Calculation	Description of wave function used
Sugiura	Simple Heitler-London wave function used. No parameter varied.
Wang	Scale factor z varied (one parameter).
Rosen	Scale factor and polarization along molecular axis (two parameters).
Hirschfelder-Linnett	Scale factor, polarization along and perpendicular to molecular axis, ionic terms (four parameters).

This integral has been discussed by Hirschfelder and others.³

In Table I we list our calculated points. In Fig. 2 we compare the energies obtained in this work with several other calculations⁴⁻⁶ and also with the experimental values.⁷ These other calculations are described briefly in Table II. It will be recalled that the calculation of James and Coolidge⁸ with a thirteen-parameter variational function led to substantially the experimental value at internuclear separation $1.4 a_0$. The parameter x leads to an appreciable lowering of the energy for internuclear separations near the minimum energy, provided z is also varied.

A test which is sometimes applied to a wave function is whether or not the virial theorem is satisfied at the condition of minimum energy.^{2,9} It is known⁹ that the Wang function, which introduces the scale factor z into the Heitler-London wave function, brings agreement with this test, whereas the original function gave serious disagreement. The use of the parameter x maintains the agreement with the virial theorem.

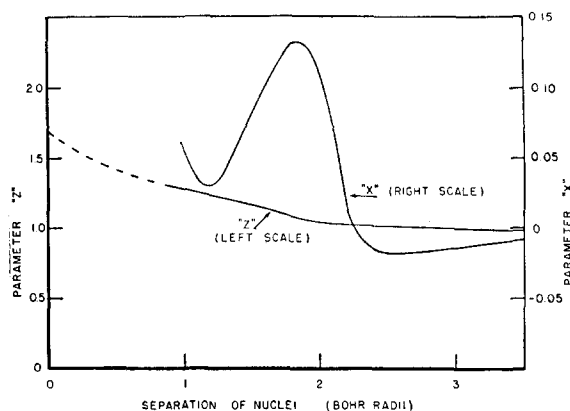


FIG. 3. Behavior of the parameters z and x as a function of distance.

³ Hirschfelder, Eyring, and Rosen, *J. Chem. Phys.* **4**, 121 (1936); J. O. Hirschfelder and C. N. Weygandt, *J. Chem. Phys.* **6**, 806 (1938).

⁴ Y. Sugiura, *Zeits. f. Physik* **45**, 484 (1927).

⁵ S. C. Wang, *Phys. Rev.* **31**, 579 (1928).

⁶ N. Rosen, *Phys. Rev.* **38**, 2099 (1931).

⁷ R. Rydberg, *Zeits. f. Physik* **73**, 376 (1931).

⁸ H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

⁹ J. O. Hirschfelder and J. F. Kincaid, *Phys. Rev.* **52**, 658 (1937).

The behavior of the two parameters z and x as a function of internuclear separation is indicated in Fig. 3. The variation of x has only a small effect on z and consequently the values of our parameter z are very close to those of the usual Wang variation. The effect of x is to increase z near the minimum. The fact that $(z-1)$ becomes negative for large values of internuclear separation is well known. In this work we found it interesting that the parameter x also changes sign for large values of R (i.e., in Fig. 1, R' becomes greater than R for large R). The dashed lines for z in Fig. 3 are interpolated. The value of z for $R=0$ is known to be 1.6875. The value of x for $R=0$ is zero. Since there are no calculated points in the interval $0 \leq R < 1$ and x ap-

parently has a maximum value in this region, we have made no attempt to sketch the curve here.

The variation of the parameter x alone in the Heitler-London wave function for H_2 brings about only a slight improvement in the energy (about 2.5 kcal/mole). We have not shown this calculation in Fig. 2. It is only with the simultaneous variation of the scale factor z that a substantial lowering of the energy is obtained. It is seen in Fig. 2 that the improvement over the Wang energy on introduction of the parameter x is about 10 kcal/mole.

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