Configuration Interaction in the Hydrogen Molecule—The Ground State*

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With the completion of computer programs for the electronic repulsion integrals,[1] it has become possible to add still another to the long and illustrious list of calculations on the hydrogen molecule. In view of the widespread use of LCAO (linear combination of atomic orbitals) molecular orbitals, there seems to be some merit in an exhaustive study to determine just how well one can do with such wave functions.

ELECTRONIC WAVE FUNCTION

We have used the method of configuration interaction here in an attempt to represent adequately the spatial correlation of electronic motions in the molecule. One can think of correlation in a two-electron diatomic molecule in three ways[2,3]—corresponding to the cylindrical coordinates ρ, θ, z: (1) in-out correlation, where the electrons tend to repel each other in such a way that one electron is close to the axis and the other further out radially; (2) angular correlation, where the two electrons tend to keep to opposite sides of an axial plane; (3) left-right correlation, where the two electrons tend to stay near different nuclei.

In the method of configuration interaction, the total electronic wave function is written as a linear combination of total electronic functions, or configurations. Often, as in this research, each configuration is represented as an antisymmetrized product of one-electron functions (spin orbitals). The individual configurations can be regarded as representing various conditions, or virtual states, of the molecule in which the Coulomb repulsion of the electrons acts predominantly in one way, corresponding to one of the coordinates ρ, θ, or z.[4]

The molecular orbitals used here are the primitive symmetry orbitals constructed from Slater-type atomic functions:

$$\sigma_g\chi, \quad \sigma_u\chi = 2^{-\frac{1}{2}}(\chi_a \pm \chi_b);$$

$$\pi_g 2p, \quad \pi_u 2p = 2^{-\frac{1}{2}}(2p\pi_a \mp 2p\pi_b),$$

with $\chi = 1s$ or $2s$ or $2p\sigma$, where

$$\left.\begin{matrix} 1s = (\zeta^3/\pi)^{\frac{1}{2}} e^{-\zeta r} \\ 2s = (\zeta^5/3\pi)^{\frac{1}{2}} r e^{-\zeta r} \end{matrix}\right\} \quad \left.\begin{matrix} 2p\sigma \\ 2p\pi \\ 2p\bar{\pi} \end{matrix}\right\} = (\zeta^5/\pi)^{\frac{1}{2}} r e^{-\zeta r} \left\{\begin{matrix} \cos\theta \\ \sin\theta e^{i\phi} \\ \sin\theta e^{-i\phi}. \end{matrix}\right.$$

Several large-scale calculations were initially carried out, with as many as 12 configurations, in an attempt to minimize the number of configurations as well as the energy. All possible configurations that can be constructed with first and second quantum shell AO's were tried. It soon became apparent that the following five-configuration wave function would do nearly as well (that is, the corresponding total energy was 0.01 to 0.02 ev poorer) as any larger one[5]:

$$\Psi = c_1(\sigma_g 1s \sigma_g 1s') + c_2(\sigma_g 2s \sigma_g 2p) + c_3(\sigma_u 1s \sigma_u 1s') + c_4(\pi_u 2p)^2 + c_5(\pi_g 2p)^2.$$

$(\sigma_g 1s \sigma_g 1s')$ is the basic configuration modified to the "open shell" form, with $\zeta_{1s} \neq \zeta_{1s'}$.[6] The first two configurations, since they tend to put one electron in an orbital close to the axis and the other in a more radially diffuse orbital, may be interpreted as accounting for the in-out correlation. The third configuration gives mostly left-right correlation, since the orbitals have a nodal plane in the center of the molecule and perpendicular to the axis. This nodal plane does the trick because upon minimizing the energy with respect to the coefficients, c_1 and c_3 come out opposite in sign. This means that Ψ, and therefore $|\Psi|^2$, is smaller in magnitude when both electrons are at the same end of the molecule, $(\sigma_u 1s\, \sigma_u 1s') > 0$, than when they are at opposite ends, $(\sigma_u 1s \sigma_u 1s') < 0$. The last two configurations represent primarily the angular correlation effect. The nodal plane here contains the axis, thus tending to keep the electrons on opposite sides of the molecule.

DISCUSSION OF RESULTS

Table I is illustrative of the kind of results that were obtained.[7] The ζ's were fully optimized only for the five-configuration wave function, IX. However, some spot adjustments of the ζ's indicated that all the results would not be substantially altered (certainly no more than 0.01 ev). With the exception of functions I and

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[1] C. C. J. Roothaan, J. Chem. Phys. **28** 982 (1958).

[2] J. E. Lennard-Jones, J. Chem. Phys. **20**, 1024 (1952).

[3] E. Callen, J. Chem. Phys. **23**, 360 (1955).

[4] The authors wish to acknowledge the impetus given to this research by a reading of a similar study of the helium atom by G. R. Taylor and R. G. Parr, Proc. Natl. Acad. Sci. U.S. **38**, 154 (1952).

[5] All configurations of the type $(\varphi\varphi')$ represent the symmetrized sum $\frac{1}{2}[\varphi(1)\varphi'(2) + \varphi'(1)\varphi(2)]$.

[6] R. Wallis, J. Chem. Phys. **23**, 1256 (1955).

[7] These calculations were done at $R = 1.40$ a.u. Energy units are 1 a.u. = 27.210 ev. Distance units are 1 a.u. = 0.52915 A.

TABLE I. Sample wave functions at equilibrium distance.

	Wave function	Binding energy (ev)
I	$(\sigma_g 1s)^2$	3.4850
II	$(\sigma_g 1s\ \sigma_g 1s')$	3.5779
III	$(\sigma_g 1s)^2$, $(\sigma_u 1s)^2$	4.0210
IV	$(\sigma_g 1s\ \sigma_g 1s')$, $(\sigma_u 1s\ \sigma_u 1s')$	4.0858
V	$(\sigma_g 1s\ \sigma_g 1s')$, $(\sigma_g 2s\ \sigma_g 2p)$, $(\sigma_u 1s\ \sigma_u 1s')$	4.2547
IV	$(\sigma_{g,u} 1s \sigma_{g,u} 1s')$, $(\sigma_{g,u} 1s\ \sigma_{g,u} 2p)$, $(\sigma_{g,u} 2s\ \sigma_{g,u} 2p)$, $(\sigma_{g,u} 2s\ \sigma_{g,u} 2s')$	4.2652
VII	$(\sigma_g 1s\ \sigma_g 1s')$, $(\pi_u 2p)^2$	3.8678
VIII	$(\sigma_g 1s\ \sigma_g 1s')$, $(\sigma_u 1s\ \sigma_u 1s')$, $(\pi_u 2p)^2$	4.3462
IX	$(\sigma_g 1s\ \sigma_g 1s')$, $(\sigma_g 2s\ \sigma_g 2p)$, $(\sigma_u 1s\ \sigma_u 1s')$, $(\pi_u 2p)^2$, $(\pi_g 2p)^2$	4.5431
X	$(\sigma_{g,u} 1s\ \sigma_{g,u} 1s')$, $(\sigma_{g,u} 1s\ \sigma_{g,u} 2p)$, $(\sigma_{g,u} 2s\ \sigma_{g,u} 2p)$, $(\sigma_{g,u} 2s\ \sigma_{g,u} 2s')$, $(\pi_{g,u} 2p)^2$	4.5505
	Experimental	4.7467

TABLE II. Numerical potential curve.

R (a.u.)	B.E. (ev)[a]	ζ_{1s}	ζ_{1s}'	ζ_{2s}	$\zeta_{2p\sigma}$	$\zeta_{2p\pi}$
0.8	0.3364	1.053	1.68	1.41	2.27	2.03
0.9	2.0679	1.035	1.635	1.36	2.20	1.97
1.0	3.1817	1.02	1.59	1.33	2.13	1.91
1.1	3.8768	1.00	1.54	1.275	2.06	1.86
1.2	4.2818	0.99	1.51	1.24	1.99	1.80
1.25	4.4047	0.984	1.485	1.22	1.97	1.78
1.3	4.4846	0.977	1.465	1.20	1.95	1.76
1.35	4.5288	0.97	1.445	1.18	1.92	1.73
1.38	4.5407	0.968	1.44	1.17	1.89	1.72
1.40	4.5431	0.965	1.43	1.16	1.87	1.71
1.42	4.5412	0.962	1.42	1.152	1.86	1.70
1.44	4.5358	0.959	1.415	1.145	1.85	1.69
1.5	4.4999	0.955	1.40	1.14	1.85	1.67
1.55	4.4496	0.95	1.38	1.125	1.82	1.65
1.6	4.3847	0.945	1.37	1.10	1.80	1.63
1.7	4.2195	0.94	1.34	1.085	1.76	1.60
1.8	4.0203	0.93	1.32	1.05	1.72	1.56
2.0	3.5646	0.92	1.275	1.01	1.65	1.50
2.2	3.0819	0.91	1.24	0.96	1.58	1.45
2.4	2.6095	0.905	1.205	0.92	1.52	1.40
2.5	2.3842	0.90	1.19	0.89	1.47	1.38
2.6	2.1687	0.90	1.178	0.87	1.44	1.36
2.7	1.9641	0.897	1.166	0.85	1.42	1.33
2.8	1.7713	0.897	1.155	0.83	1.39	1.31
2.9	1.5908	0.899	1.145	0.812	1.37	1.30
3.0	1.4230	0.90	1.136	0.795	1.35	1.28
3.1	1.2680	0.90	1.129	0.78	1.32	1.26
3.2	1.1256	0.90	1.12	0.76	1.31	1.24
3.3	0.9955	0.901	1.113	0.742	1.29	1.22
3.4	0.8774	0.902	1.106	0.73	1.27	1.21
3.5	0.7707	0.905	1.10	0.71	1.24	1.20
3.6	0.6749	0.908	1.095	0.70	1.23	1.19
3.7	0.5893	0.912	1.09	0.685	1.22	1.17
3.8	0.5130	0.917	1.086	0.66	1.18	1.16
3.9	0.4455	0.92	1.08	0.64	1.16	1.15
4.0	0.3859	0.924	1.076	0.62	1.14	1.14
4.2	0.2878	0.93	1.069	0.59	1.10	1.12
4.4	0.2130	0.94	1.06	0.56	1.06	1.09
4.6	0.1569	0.948	1.05	0.53	1.02	1.06
4.8	0.1149	0.955	1.04	0.51	0.98	1.04
5.0	0.0838	0.96	1.04	0.5	0.94	1.03
5.25	0.0563	0.965	1.032	0.5	0.89	1.01
5.5	0.0377	0.97	1.028	0.5	0.85	1.0
5.75	0.0252	0.975	1.022	0.5	0.81	0.985
6.0	0.0168	0.98	1.02	0.5	0.78	0.975

TABLE II.—*Continued.*

R	C_1	C_2	C_3	C_4	C_5
0.8	0.2757	0.0258	−0.1795	−0.0244	−0.0344
0.9	0.2789	0.0267	−0.1712	−0.0253	−0.0311
1.0	0.2819	0.0276	−0.1661	−0.0263	−0.0287
1.1	0.2848	0.0286	−0.1648	−0.0271	−0.0267
1.2	0.2884	0.0292	−0.1628	−0.0279	−0.0255
1.25	0.2898	0.0294	−0.1632	−0.0282	−0.0247
1.3	0.2914	0.0294	−0.1638	−0.0285	−0.0241
1.35	0.2930	0.0296	−0.1648	−0.0289	−0.0237
1.38	0.2942	0.0300	−0.1647	−0.0290	−0.0233
1.4	0.2946	0.0302	−0.1654	−0.0292	−0.0232
1.42	0.2951	0.0302	−0.1661	−0.0293	−0.0230
1.44	0.2959	0.0302	−0.1666	−0.0294	−0.0229
1.5	0.2984	0.0298	−0.1676	−0.0297	−0.0222
1.55	0.2998	0.0299	−0.1694	−0.0299	−0.0218
1.6	0.3019	0.0298	−0.1708	−0.0301	−0.0215
1.7	0.3053	0.0296	−0.1742	−0.0304	−0.0206
1.8	0.3093	0.0294	−0.1786	−0.0307	−0.0200
2.0	0.3166	0.0300	−0.1883	−0.0310	−0.0187
2.2	0.3240	0.0272	−0.1998	−0.0308	−0.0174
2.4	0.3309	0.0255	−0.1666	−0.0304	−0.0161
2.5	0.3341	0.0245	−0.2197	−0.0300	−0.0154
2.6	0.3373	0.0237	−0.2265	−0.0296	−0.0147
2.7	0.3404	0.0225	−0.2339	−0.0291	−0.0142
2.8	0.3433	0.0215	−0.2410	−0.0285	−0.0135
2.9	0.3462	0.0203	−0.2480	−0.0278	−0.0127
3.0	0.3488	0.0192	−0.2552	−0.0270	−0.0120
3.1	0.3511	0.0181	−0.2623	−0.0262	−0.0112
3.2	0.3531	0.0168	−0.2694	−0.0254	−0.0105
3.3	0.3549	0.0156	−0.2762	−0.0245	−0.0098
3.4	0.3564	0.0144	−0.2827	−0.0236	−0.0090
3.5	0.3578	0.0133	−0.2888	−0.0226	−0.0083
3.6	0.3590	0.0123	−0.2946	−0.0216	−0.0076
3.7	0.3599	0.0113	−0.3000	−0.0206	−0.0069
3.8	0.3606	0.0105	−0.3050	−0.0196	−0.0062
3.9	0.3610	0.0095	−0.3098	−0.0186	−0.0055
4.0	0.3614	0.0086	−0.3141	−0.0177	−0.0049
4.2	0.3616	0.0071	−0.3219	−0.0158	−0.0038
4.4	0.3614	0.0058	−0.3280	−0.0141	−0.0028
4.6	0.3608	0.0046	−0.3332	−0.0126	−0.0020
4.8	0.3600	0.0036	−0.3373	−0.0112	−0.0013
5.0	0.3594	0.0030	−0.3406	−0.0098	−0.0007
5.25	0.3585	0.0021	−0.3439	−0.0085	−0.0001
5.5	0.3577	0.0015	−0.3463	−0.0073	0.0003
5.75	0.3569	0.0010	−0.3481	−0.0063	0.0006
6.0	0.3563	0.0007	−0.3493	−0.0054	0.0008

[a] Units are 1 a.u.=27.210 ev.

III, the ζ's used are those of Table II for $R=1.4$. Wave functions I and III are the Coulson MO function[8] and the Weinbaum function, respectively,[9,10] and they are included for comparison purposes. A comparison of functions V and VI, and IX and X, illustrates the saturation effect achieved with first and second quantum shell functions. Clearly, the extra configurations in the longer expansions are unimportant, and evidently one must add higher quantum shell functions to obtain further improvement. We intend to do this in the near future as the appropriate integrals programs become available. We expect the greatest improvement to come from the addition of a function containing $3d\delta$,

[8] C. A. Coulson, Trans. Faraday Soc. **33**, 1479 (1937).
[9] S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).
[10] The discrepancy of 0.02 ev between these authors and our results is due to our use of the most recent fundamental constants. Results in atomic units are the same.

which should serve to bolster the angular correlation. Possibly the next most important would be $3d\sigma$.

The open-shell forms $(\sigma 1s\, \sigma 1s')$ do not improve matters much—about 0.08 ev, as found also by Wallis.[6] The total improvement due to the "in-out correlation" configurations seems to be about 0.25 ev (compare III and VI). Comparison of functions I–VI with VII–X indicates that the angular correlation accounts for at least 0.3 ev of the energy. The greatest improvement ($\approx$0.5 ev) comes from the "left-right correlation" effect (compare functions II and IV). The convergence of the energy from functions I to VI is consistent with the estimate of James and Coolidge of 4.30 ev as the limit for trial functions which do not take into account

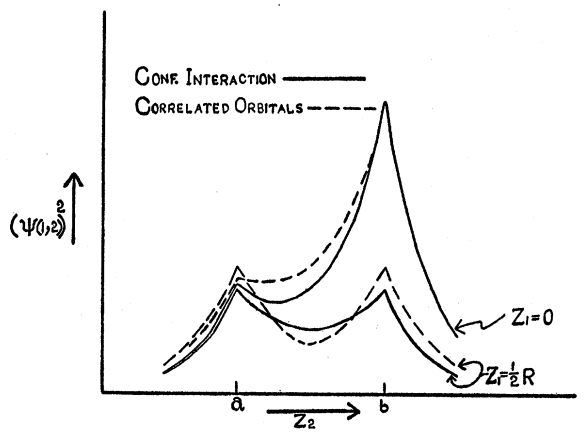

FIG. 1. Probability density vs interelectronic distance along the molecular axis. $Z_1=0$ at center a.

angular correlation.[11] It is also consistent with Callen's result of 4.276 ev, using a three configuration function without angular terms.[3]

Figures 1 and 2 illustrate the effects of left-right and angular correlation, respectively, for our five-configuration function IX. In Fig. 1, we have plotted $|\Psi|^2$ along the axis for two cases: (1) electron 1 is fixed on one nucleus, (2) electron 1 is fixed in the center of the molecule. For comparison, we have also included the corresponding plots for the "correlated orbitals" wave function.[12] In Fig. 2, we have plotted the wave function itself against $(\phi_1-\phi_2)$. An estimate of the "correlation cusp" one should obtain has also been drawn for comparison. Inclusion of higher angular terms would be expected to effect a better approximation to such a cusp behavior.

Of the other configurations tried but not indicated in the table, $(\sigma_g 1s\, \sigma_g 2s)$, $(\sigma_u 1s\, \sigma_u 2s)$, $(\sigma_g 2p\, \sigma_g 2p')$, and $(\sigma_u 2p\, \sigma_u 2p')$ were found to contribute practically nothing ($<$0.01 ev). The configuration $(\sigma_g 1s\, \sigma_g 2p)$, when used in place of $(\sigma_g 2s\, \sigma_g 2p)$, was found to provide

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

[12] Correlated wave functions of the form $\Psi=\varphi(1)\varphi(2)\chi(r_{12})$ and $\Psi=[\varphi(1)\psi(2)+\psi(1)\varphi(2)]\chi(r_{12})$ recently have been computed for H_2 by W. Kolos (private communication).

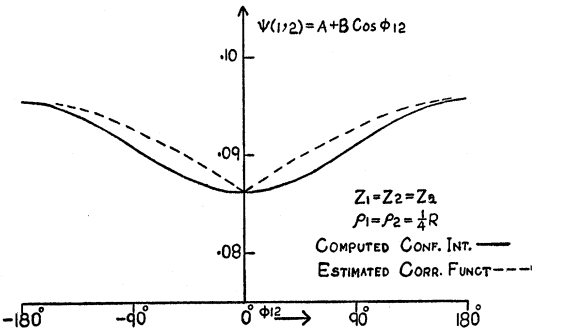

FIG. 2. Dependence of the total wave function on the relative angular coordinate.

a substantial improvement, although less than $(\sigma_g 2s\, \sigma_g 2p)$ by $\approx$0.03 ev. The two together did essentially no more than $(\sigma_g 2s\, \sigma_g 2p)$ alone. The open-shell configurations $(\pi_g 2p\, \bar{\pi}_g 2p')$ and $(\pi_u 2p\, \bar{\pi}_u 2p')$ were also tried and found to be of inappreciably greater value than the closed-shell $(\pi 2p)^2$ forms. An attempt was also made to make $\zeta_g 1s \pm \zeta_u 1s$ for the functions $(\sigma_g 1s)^2+\alpha(\sigma_u 1s)^2$ and $(\sigma_g 1s)^2+\alpha(\sigma_u 1s)^2+\beta(\sigma_g 1s\, \sigma_g 2p)$, independently varying ζ_g and ζ_u to minimize the energy. The minimum energy, for all practical purposes, was found to be at $\zeta_g=\zeta_u$. For example, for the first function, the best binding energy was 4.02111 ev at $\zeta_g=1.201$, $\zeta_u=1.190$, whereas $\zeta_g=\zeta_u=1.20$ gave 4.02101 ev.

DETAILS OF THE CALCULATION

As mentioned earlier, the ζ's were optimized for the five-configuration function. This was done in a stepwise fashion. Fixing ζ_{2s}, $\zeta_{2p\sigma}$, $\zeta_{2p\pi}$, the energy was computed over a two-dimensional grid of ζ_{1s}, $\zeta_{1s'}$ values. The best ζ pair was then found by quadratic interpolation.

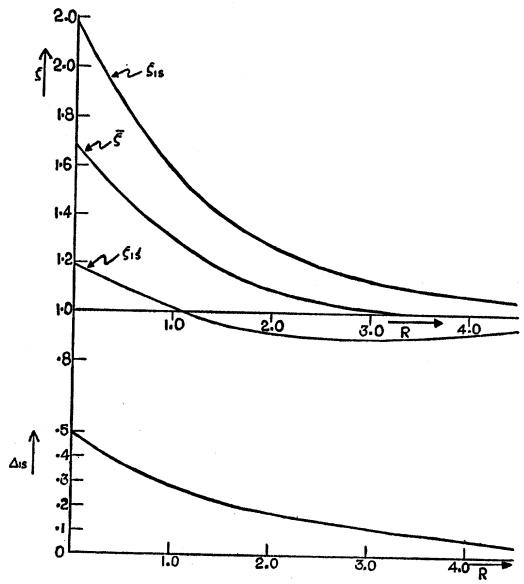

FIG. 3. Optimum ζ vs R for the $1s$ and $1s'$ functions. $\bar{\zeta}=\frac{1}{2}(\zeta_{1s}+\zeta_{1s'})$ $\Delta_{1s}=\zeta_{1s}-\zeta_{1s'}$.

Fixing ζ_{1s} and $\zeta_{1s'}$ at these values, the process was repeated for ζ_{2s} and $\zeta_{2p\sigma}$. With these values fixed, the energy was then minimized with respect to $\zeta_{2p\pi}$.

This procedure can be justified on the basis of the experience obtained from minimizing the energy over a range of R values (see next section). For several values of R, this stepwise minimization was repeated a second time, and the results were found to be self-consistent to at least three significant figures in the binding energy. Furthermore, the ζ's of the various orbitals turned out to be fairly independent, e.g., the best $1s\zeta$'s were nearly the same (to within 0.01) for function IV as for function IX (Table I). Similar results were found for the $2s$ and $2p\zeta$'s for functions V and IX. We estimate the error in the energy due to incomplete minimization with respect to the ζ's to be no greater than 0.005 ev at all values of R. All the integrals were obtained to an accuracy of six significant figures.

A potential energy curve was computed with the five-configuration function, IX, optimizing the ζ's at each point along the curve. The best ζ's were obtained for $R=1.0$, 1.4, 2.0, 2.5, 3.5, and 5.0 in the manner described previously. Curves of ζ vs R were then drawn, and the ζ's for all other R values were read off from these curves (see Figs. 3 and 4). The $1s$ ζ curves are estimated to be accurate to 0.01, and the $2s$ and $2p$ curves are probably accurate to 0.03. The energy is much less sensitive to the $2s$ and $2p\zeta$'s than to the $1s$. The effect of adding in the $(\sigma_u 2s\, \sigma_u 2p)$ configuration also was investigated for several R values. The energy was changed by no more than 5 parts in 1000. In Fig. 3, we have also plotted the quantity $\bar{\zeta}=\frac{1}{2}(\zeta_{1s}+\zeta_{1s}')$, which turns out to be practically identical with Coulson's ζ values for the function $(\sigma_g 1s)^2$.[8]

The binding energy was computed at 45 different

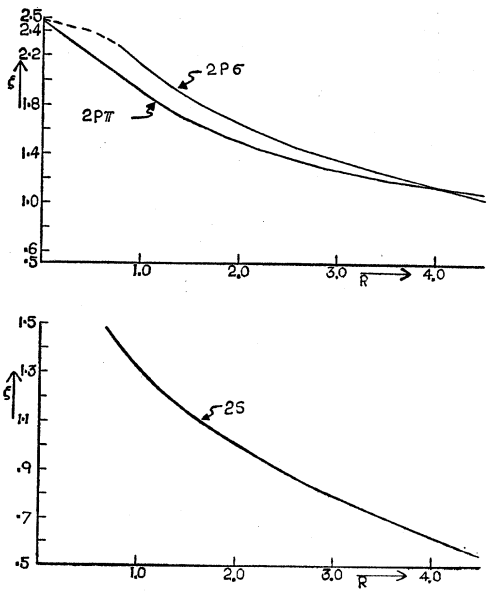

FIG. 4. Optimum ζ vs R for the $2s$, $2p\sigma$, and $2p\pi$ functions.

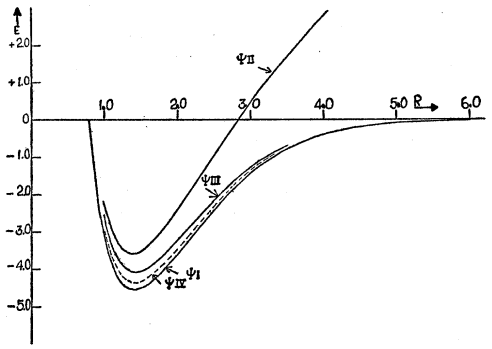

FIG. 5. Binding energy vs R for the wave functions
$\Psi_{\rm I}=(\sigma_g 1s\, \sigma_g 1s')+(\sigma_g 2s\, \sigma_g 2p)+(\sigma_u 1s\, \sigma_u 1s')+(\pi_u 2p)^2+(\pi_g 2p)^2$,
$\Psi_{\rm II}=(\sigma_g 1s\, \sigma_g 1s')$,
$\Psi_{\rm III}=(\sigma_g 1s\, \sigma_g 1s')+(\sigma_u 1s\, \sigma_u 1s')$,
$\Psi_{\rm IV}=(\sigma_g 1s\, \sigma_g 1s')+(\sigma_u 1s\, \sigma_u 1s')+(\pi_u 2p)^2+(\pi_g 2p)^2$.

values of the internuclear distance, from $R=0.8$ to $R=6.0$. The results are tabulated in Table II and the resulting curve drawn in Fig. 5. We have also drawn, on the same graph, the curves for several other functions which omit various configurations. While the ζ's are not fully optimized for these functions, it is doubtful that the results would be substantially different.

A quadratic curve was fitted to the points $R=1.38$, 1.40, 1.42. This gave an interpolated binding energy of 4.54306 ev at $R=1.4013$, compared with the experimental value of 4.7467 ev at $R_{\min}=1.4008$.

CALCULATION OF SPECTROSCOPIC CONSTANTS

Dunham,[13] in a study of the energy levels of a rotating vibrator, solved the Schrödinger equation for the problem, namely,

$$\frac{d^2\psi}{d\xi^2}+\frac{2\mu r_e^2}{h^2}\left[E-V-\frac{h^2K(K+1)}{2\mu r_e^2(1+\xi^2)}\right]\psi=0,$$

where $\xi=(r-r_e)/r_e$, μ is the reduced mass, K the rotational quantum number, and V is a potential energy with a minimum at r_e, expanded in a power series around $\xi=0$ as indicated in the equation

$$V=hca_0\xi^2(1+a_1\xi+a_2\xi^2+\cdots). \qquad (1)$$

In Eq. (1) the quantity a_0 is equal to $\omega_e^2/4B_e$ where ω_e is the classical harmonic oscillator frequency for small displacement expressed in cm^{-1}; $B_e=h/8\pi^2\mu r_e^2 c$. is the rotational constant for a rigid rotator with moment of inertia μr_e^2.

Dunham gives the solution as the double sum

$$F_{vK}=\sum_{lj}Y_{lj}(v+\tfrac{1}{2})^l K^j(K+1)^j, \qquad (2)$$

where v and K are the vibrational and rotation quantum numbers, respectively. In Eq. (2) the coefficients Y_{lj} are expressed in terms of the harmonic oscillator and rigid rotator constants ω_e and B_e and the coefficients

[13] J. L. Dunham, Phys. Rev. **41**, 721 (1931).

TABLE III.[a] Spectroscopic constants.

	Computed	Exptl.[b]
Y_{10}	4385	4401
Y_{20}	−115	−121
Y_{30}	−1.57	0.72
Y_{01}	60.81	60.86
Y_{11}	−3.064	−3.017

[a] Units are cm^{-1}.
[b] See reference 14.

of Eq. (1). These coefficients Y_{lj} are related to the experimentally observed spectroscopic constants. It requires a very careful analysis to determine exactly what the coefficients Y_{lj} experimentally compare to. (For details see Dunham[13] and Stoicheff.[14]) However, to high accuracy (better than 99.9%) the identification indicated in Eqs. (3) can be made. Note that the ω_e and B_e of Eqs. (3) are experimental quantities and are not to be confused with the harmonic oscillator and rigid rotator constants just defined.

$$Y_{10}=\omega_e, \quad Y_{20}=-\omega_e x_e, \quad Y_{30}=\omega_e y_e, \quad Y_{01}=B_e, \quad Y_{11}=-\alpha_e. \tag{3}$$

An eighth-degree polynomial was fitted to the potential energy curve computed using the five-configuration wave function of Table II for the internuclear distances $r=0.9$, 1.1, 1.3, 1.4, 1.5. 1.7, 2.0, 2.4, 2.8 a.u. When transformed to the form of Eq. (1), the coefficients a_n were found to be

$$a_0=0.79178, \quad a_1=-1.607, \quad a_2=1.957, \quad a_3=-2.278, \quad a_4=1.956, \quad a_5=-0.817, \quad a_6=0.070.$$

In Table III the comparisons between the computed Y_{lj} using these coefficients and the spectroscopic constants by Stoicheff[14] are shown.

In the course of this research, a crude bibliography of previous work on the H_2 ground state seemed to grow quite naturally, and it was thought that it might be of some value to expand it and include it in the current report. All results have been standardized and brought up to date with the most recent values of the fundamental constants. A capsule description of each calculation is included. Only those calculations have been included which represent a direct evaluation of the expectation value of the energy, thus eliminating perturbation calculations, semiempirical calculations, etc. While this Bibliography pretends to be complete, it probably is not; we can only plead that the literature on this subject is too extensive to preclude omissions.

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BIBLIOGRAPHY OF HYDROGEN MOLECULE CALCULATIONS

Reference	B.E.[a]	R	Details of calculation
W. Heitler and F. London, Z. Physik **44**, 455 (1927) Y. Sugiura, Z. Physik **45**, 484 (1927)	3.20[b]	0.80 A	$\Psi=1s_a1s_b+1s_b1s_a$. $\zeta=1.0$, $\nu=4800$ cm^{-1}—fitted quadratic curve to several points computed with this ζ.
S. Wang, Phys. Rev. **31**, 579 (1928)	3.782 (0.139)	1.406 a.u.	$\Psi=1s_a1s_b+1s_b1s_a$. Varied ζ, $\zeta=1.166$. $\nu=4900$ cm^{-1}—fitted quadratic to several points computed with fixed ζ.
E. Hylleraas, Z. Physik **71**, 739 (1931)	3.4201[c] (0.12571)	1.40 a.u.	$\Psi=1s\sigma\ 1s\sigma'+1s\sigma'1s\sigma$, where $1s\sigma$ and $1s\sigma'$ are 1st terms of H_2^+ solutions for $Z=1$ and 0.5, respectively.
N. Rosen, Phys. Rev. **38**, 2099 (1931)	4.04 (0.1485)	1.416 a.u.	$\Psi=\psi_a\psi_b+\psi_b\psi_a$, where $\psi=1s+\lambda 2p\sigma$. $\zeta_{1s}=\zeta_{2p}=1.19$. Finds $\lambda=0.105$. Draws potential curve, gets $\nu=4260$ cm^{-1} from Morse curve fit. In comparing with experiment, forgets to include zero-point vibrational energy.
S. Weinbaum, J. Chem. Phys. **1**, 593 (1933)	4.024 (0.1479)	1.42 a.u.	$\Psi=c(1s_a1s_b+1s_b1s_a)+(1s_a1s_a+1s_b1s_b)$. $c=3.9$, $\zeta=1.193$, fits Morse curve, $\nu=4750$ cm^{-1}. Minimizes covalent and ionic ζ's independently, finds $\zeta_c=\zeta_i$.
	3.230 (0.1187)	1.67 a.u.	Same function but $\zeta=1.0$, $c=6.322$ with no ionic (repeat Sugiura), gets 3.145 ev (0.1156).
	4.122 (0.1515)	1.41 a.u.	Same function, except $1s+\sigma 2p\sigma$ replaces $1s$ in the covalent part. Best $\zeta=1.190$, $c=5.7$, $\sigma=0.07$.

[a] Binding energies in a.u. are in () when available. All binding energies are in ev corrected when possible to 1 a.u.=27.210 ev.
[b] Has been recalculated by Coulson; see Coulson (1937).
[c] Computed by Wallis and Hulbert from Hylleraas' formulas.

[14] B. P. Stoicheff, Can. J. Phys. **35**, 730 (1957).

Reference	B.E.[a]	R	Details of calculation
H. James and A. Coolidge, J. Chem. Phys. **1,** 825 (1933)	4.7200[d] (0.173465)	1.40 a.u.	$\Psi=\exp[-\delta(\xi_1+\xi_2)]\Sigma_{mnjkp}c_{mnjkp}[\xi_1^m\xi_2^n\eta_1^{2j}\eta_2^{2k}r_{12}^p+\xi_1^n\xi_2^m\eta_1^{2k}\eta_2^{2j}r_{12}^p]$, 13 terms, $\delta=0.75$. Draws potential curve for an 11-term function.
	4.2910 (0.1577)	1.40	Without r_{12} terms, not minimizing coefficients.
T. Nagamiya, Proc. Phys.-Math. Soc. Japan, **18,** 497 (1936)	4.215 (0.1549)	1.40 a.u.	$\Psi=\exp[-\alpha(\xi_1+\xi_2)][1+c_1(\xi_1+\xi_2)+c_2\eta_1\eta_2+c_3[P_2^0(\eta_1)+P_2^0(\eta_2)]+c_4[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\frac{1}{2}}\cos(\phi_1-\phi_2)]$. Sets $\alpha=0.75$. Makes the claim that odd powers of r_{12} are unnecesesary in James and Coolidge function.
C. A. Coulson, Trans. Faraday Soc. **33,** 1479 (1937)	3.488	0.732 A	$\Psi=\varphi(1)\varphi(2)$, when $\varphi=1s_a+1s_b=\sigma_g1s$. Best $\zeta=1.197$, $\nu=4584$ cm^{-1}. Fits Morse curve to 3 points, ζ minimized for each. Points out potential curve very sensitive to small errors in energy. Plots best ζ vs R. Recalculates work of Wang, Rosen, Sugiura. Corrects Sugiura to 3.156 ev at 0.869 A. Corrects Wang ν to $\nu=4180$. (Wang used same ζ along potential curve.)
H. Hellman, *Einfuhrung in die Quantenchemie* (1937), p. 133	2.65	1.6	$\Psi=\sigma_g1s(1)\sigma_g1s(2)$ $\sigma\delta1s=1s_a+1s_b$. $\zeta=1.0$.
C. A. Coulson, Proc. Cambridge Phil. Soc. **34,** 204 (1938)	3.6239 (0.13318)	1.40	$\Psi=\varphi(1)\varphi(2)$, $\varphi=\exp(-\delta\xi)\Sigma_{mn}c_{mn}\xi^m\eta^{2n}$, 5 terms setting $\delta=0.75$. For 2 terms (η^2) gets 3.1142 (0.11445), 3 terms (η^2, ξ) gets 3.5559 (0.13068).
T. Inui, Proc. Phys.-Math. Soc. Japan **20,** 770 (1938); ibid. **23,** 992 (1941)	4.0584 (0.14915)	1.44	$\Psi=\varphi\psi+\psi\varphi$, where φ, $\psi=\exp(-\alpha\xi+\beta\eta)$. Best $\alpha=0.8735$, $\beta=0.6855$. $\nu=4390$ cm^{-1}. Fits Morse curve, finds min at 1.440 with B.E=. 4.0584 (0.14915).
A. Nordsieck, Phys. Rev. **58,** 310 (1940)	4.05 (0.149)	1.40	$\Psi=\varphi\psi+\psi\varphi$; φ, $\psi=\exp(-\frac{1}{2}A\xi\pm\frac{1}{2}B\eta)$. $A=1.706$, $B=1.344$. Repeats Inui, only not as well minimized. Compares electron density at various points in molecule for Wang, J and C, and Nordsieck functions.
E. Ishiguro, J. Phys. Soc. Japan **3,** 129 (1948)	4.262	1.40	$\Psi=\exp[-\delta(\xi_1+\xi_2)][c_1+c_2(\eta_1^2+\eta_2^2)+c_3\eta_1\eta_2+c_4(\xi_1+\xi_2)+c_5(\xi_1^2+\xi_2^2)+c_6\xi_1\xi_2\eta_1\eta_2+c_7M\cos(\phi_1-\phi_2)]$, where $M=[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\frac{1}{2}}$. Sets $\delta=0.75$. Draws potential curve.
J. Hirschfelder and J. Linnett, J. Chem. Phys. **18,** 130 (1950)	4.2506[e]	1.455	$\Psi=1s_a1s_b[1+(\alpha\zeta^2)(x_ax_b+y_ay_b)+(\beta\zeta^2)z_az_b]+1s_a1s_b[1+(\alpha\zeta^2)(x_bx_a+y_by_a)+(\beta\zeta^2)z_bz_a]+\epsilon[1s_a1s_a+1s_b1s_b]$. x_a, y_a, etc. are Cartesian coordinates of electrons. Best $\zeta=1.195$, $\alpha=-0.05735$, $\beta=-0.06944$, $\epsilon=0.3334$. Makes extensive plot of potential curve including Van der Waal's region. Discusses behavior of parameters along curve.
E. Gurnee and J. Magee, J. Chem. Phys. **18,** 142 (1950)	4.126[f]	1.5	$\Psi=1s_c1s_d+1s_d1s_c$, where the centers c and d are inside the molecule at a distance x from the nuclei. Best $\zeta=1.16$, $x=0.08$. At $R=1.4$, B.E.$=4.108$, $\zeta=1.185$, $x=0.06$. $x<0$ for large R, and varies wildly with R.
G. Newell, Phys. Rev. **78,** 711 (1950)	4.5661 (0.16781)	1.40	$\Psi=\exp[-\frac{1}{2}\alpha(\xi_1+\xi_2)]\{\cosh\frac{1}{2}\beta(\eta_1-\eta_2)+a\exp[-\frac{1}{2}\delta(\xi_1+\xi_2)]M\cdot\cos(\phi_1-\phi_2)+b\eta_1\eta_2+c[\xi_1-(4/\alpha)][\xi_2-(4/\alpha)]\}$, where $M=[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\frac{1}{2}}$. Best $\alpha=1.727$, $\beta=1.435$, $\delta=0.817$. Draws coarse potential curve.
A. Frost and J. Braunstein, J. Chem. Phys. **19,** 1133 (1951)	4.109 (0.151)	1.34	$\Psi=\sigma_g1s\sigma_g1s(1+pr_{12})$. Best $\zeta=1.285$, $p=0.28$.
C. Mueller and H. Eyring, J. Chem. Phys. **19,** 1495 (1951)	4.20	?	$\Psi=\varphi\psi+\psi\varphi$, where $\varphi=x_a+\epsilon x_b$; $\psi=\epsilon x_a+x_b$, where $x_{a,b}=\exp(-\alpha\xi\mp\beta\eta)$, i.e., "distorted" atomic orbitals. Best $\alpha=0.835$, $\beta=0.775$, $\epsilon=0.137$.
R. Wallis and H. Hulbert, J. Chem. Phys. **22,** 774 (1954)	3.68344 (0.135371)	1.40	$\Psi=\varphi\varphi'+\varphi'\varphi$, where φ, φ' are 1st two terms of H_2^+ solutions for $Z=1$, $Z'=0.5$.
	3.48451 (0.12806)	1.40	Same functions but best $Z=Z'=0.78868$.
A. Hurley, Proc. Roy. Soc. (London) **A226,** 179 (1954)	4.14 (0.152)	1.44	$\Psi=1s_c1s_d+1s_d1s_c$, c and d inside molecule distance x. Same ζ and x as Gurnee and Magee. Corrects G and M at large R.
	3.65 (0.134)	1.38	$\Psi=\varphi(1)\varphi(2)$, where $\varphi=1s_c+1s_d$, c and d as previously.
F. Berencz, Acta. Phys. Acad. Sci. Hung. **4,** 149 (1954)	4.14 (0.152)	1.338	$\Psi=[1s_a1s_b+1s_b1s_a+\epsilon(1s_a1s_a+1s_b1s_b)](1+pr_{12})$. Best $\zeta=1.248$, $\epsilon=0.356$, $p=0.073$.
R. Pauncz, Acta Phys. Acad. Sci. Hung. **4,** 237 (1954)	3.23	1.589	$\Psi=1s_a1s_b+1s_b1s_a+\lambda[\varphi_a(1,2)+\varphi_b(1,2)]$ hydrogen $1s(\zeta=1)$. $\varphi(1,2)$ is 3-term Hylleraas function for H^-. $\varphi=\exp[-\zeta(r_1+r_2)]\cdot[1+c_1r_{12}+c_2(r_1-r_2)^2]$. This is a *fully* theoretical Moffit calculation.

[d] 4.7210 is a correction given in a later communication.

[e] Energies and R too high by 0.03 and 0.04, respectively. See H. Shull and D. Ebbing, J. Chem. Phys. **28,** 866 (1958).

[f] Recomputed by H. Shull and D. Ebbing, J. Chem. Phys. **28,** 866 (1958). Discrepancy.

Reference	B.E.[a]	R	Details of calculation
B. Kockel, Ann. Physik **15**, 64 (1955)	4.30[g] (0.158)	1.46	$\Psi=\exp[-\alpha(\xi_1+\xi_2)][1+cP_2^0(\eta_1)]^{\frac{1}{2}}[1+cP_2^0(\eta_2)]^{\frac{1}{2}}$. Best $\alpha=0.875$ $c=0.48$.
	3.05 (0.112)	1.326	Repeats same for "floating" functions, finds same B.E. $\Psi=\exp[-\beta(\xi_1+\xi_2)]$, Best $\beta=0.81$.
E. Callen, J. Chem. Phys. **23**, 360 (1955)	4.1249	1.40	$\Psi=a(g)^2+b(u)^2$, where $g=\exp(-\alpha\xi)[1+A\eta^2+B\xi]$ (from Coulson) and $u=\exp(-\alpha'\xi)\eta[1+c\eta^2+D\xi]$. $\alpha_g=\alpha_u=0.75$. Set α_g to Coulson value.
	4.2756	1.40	$\Psi=ag^2+bu^2+c[g_ug_e+g_eg_u]$, where $g_i=(P_i-\xi)\exp(-\alpha_i\xi)$. P_i chosen to make orthog to Coulson g. $\alpha_{i,u}=1$, 0.5.
R. Wallis, J. Chem. Phys. **23**, 1256 (1955)	3.566	1.40	$\Psi=\sigma_g1s\sigma_g1s'$. Best $\zeta=1.5$, $\zeta'=0.9$.
	3.866	1.40	$\Psi=1s_a1s_b'+1s_b1s_a'+1s_a'1s_b+1s_b'1s_a$. Best $\zeta=1.4$, $\zeta'=0.9$.
	4.082	1.40	$\Psi=1s_a1s_b'+1s_b1s_a'+1s_a'1s_b+1s_b'1s_a+\lambda[1s_a1s_a'+1s_b1s_b'+1s_a'1s_a+1s_b'1s_b]$. Best $\zeta=1.4$, $\zeta'=1.0$, $\lambda=0.2584$.
A. Rahman, Current Sci. (India) **24**, 370 (1955)	3.7101 (0.13635)	1.40	$\Psi_1=\exp[-\delta(\xi_1+\xi_2)][1+p(\xi_1+\xi_2)+r\xi_1\xi_2](1+c\eta_1^2)(1+c\eta_2^2)$. $\delta=0.75$, $p=0.01134$, $r=-0.03693$, $c=0.255$.
	4.3264 (0.1590)	1.40	$\Psi=\Psi_1+\exp[-\delta(\xi_1+\xi_2)]\{[a\eta_1\eta_2+b[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)\cdot(1-\eta_2^2)]^{\frac{1}{2}}\cos(\phi_1-\phi_2)\}$. Same parameter values as before.
S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **15**, 501 (1956)	3.7999	1.4	Single-center Slater functions at center of molecule. $\Psi=\phi_1^2+c_1\varphi_1\varphi_2+c_2\varphi_2^2$, where $\varphi_1=1s+a4s$, $\varphi_2=4d$, $\zeta_{1s}=1.0$, $\zeta_{4s}=\zeta_{4d}=4.3$, $a=0.25$.
A. Rahman, Physica **23**, 31 (1957)	3.725 (0.1369)	1.35	$\Psi_1=\exp[-\delta(\xi_1+\xi_2)][1+c\eta_1^2)(1+c\eta_2^2)][1+a(\xi_1+\xi_2)+b(\xi_1\xi_2)]$. $\delta=0.75$, $c=0.25$.
	4.341 (0.15955)	1.35	$\Psi=\Psi_1+\exp[-\delta(\xi_1+\xi_2)]\{c\xi_1\xi_2\eta_1\eta_2+d\eta_1\eta_2+M\cos(\phi_1-\phi_2)\}$, where $M=[(\xi_1^2-1)(\xi_2^2-1)(1-\eta_1^2)(1-\eta_2^2)]^{\frac{1}{2}}$; same parameters.
H. Aghajanian, Mass. Inst. Technol. Quart. Progr. Rept. 12 (April 15, 1957)	4.04	1.49	$\Psi=\Sigma_{ij}c_{ij}\phi_{ij}$, where $\phi_{ij}=\chi_i\chi_j\pm\chi_j\chi_i$, where χ_i are LCAO SCF solutions $1s$, $2s$, $2p\sigma$, $2p\pi$. Omitted configuration $3\sigma_u1\sigma_u$, $3\sigma_u2\sigma_u$, $3\sigma_u3\sigma_u$. $\nu=5728$ cm^{-1}. Energy obtained as a min of Morse curve (1.0 intervals).
F. Harris, J. Chem. Phys. **27**, 812 (1957)	4.160	0.793 A	$\Psi_1=\varphi\varphi'+\varphi'\varphi$, where $\varphi=\exp(-\delta\xi-\alpha\eta)$. $\delta=0.7$, $\delta'=1.1$, $\alpha=0.7$, $\alpha'=-0.7$ (min).
	4.440	0.793 A	$\Psi=\Psi_1+c(\bar{\phi}\bar{\phi}'+\bar{\phi}'\bar{\phi})$ $\bar{\phi}=\exp(-\delta\xi-\bar{\alpha}\eta)[(\xi^2-1)(1-\eta^2)]^{\frac{1}{2}}\exp(i\phi)$. Ψ_1 parameters same. Second configuration $\delta=\delta'=1.3$, $\alpha=\alpha'=0.0$.
F. Berencz, Acta Phys. Acad. Sci. Hung. **6**, 149 (1957)	3.93	0.72 A	$\Psi=(1s_a1s_b+1s_b1s_a)(1+pr_{12})$. Best $\zeta=1.188$, $p=0.5$.
F. Berencz, Acta Phys. Acad. Sci. Hung. **6**, 423 (1957)	3.60	0.76 A	$\Psi=\varphi(1)\varphi(2)$, where $\varphi=\exp(-\alpha\xi)[\exp(-\beta\eta)+\exp(\beta\eta)]$. Best $\alpha=0.855$, $\beta=0.753$.
	4.26	0.76 A	$\Psi=\varphi(1)\varphi(2)(1+pr_{12})$, where $\varphi=\exp(-\alpha\xi)[\exp(-\beta\eta)+\exp(\beta\eta)]$. Best $\alpha=0.925$, $\beta=0.84$, $p=0.32$.
H. Aghajanian, Mass. Inst. Technol. Quart. Progr. Rept. 29 (July 15, 1957)	3.69	1.36	$\Psi_i=\varphi(1)\varphi(2)$, where $\varphi=\sigma_g1s+c_1\sigma_g2_s+c_2\sigma_g2p$. LCAO SCF, one determinant, varies scale factor.
	4.30	1.39	$\Psi=\Sigma_{ij}c_{ij}\psi_i\psi_j$ 11-configuration LCAO SCF MO's. $\nu=4747.3$ cm^{-1} from cubic fit. Omits 3 configurations (see other).
H. Joy and R. Parr, J. Chem. Phys. **28**, 448 (1958)	4.3218 (0.15883)	1.40	$\Psi_1=c_1ss'+c_2s''s'''+c_3s^{iv}d_0+c_4s^vg_0+c_5p_0^2+c_6p_{+1}p_{-1}+c_7p_0'f_0$. Single-center Slater functions at center of molecule, noninteger principle quantum numbers.
	4.3441 (0.15965)	1.40	$\Psi=\Psi_1+c_8s^{vi}d_0'+c_9d_2d_{-2}+c_{10}[(p_1'f_{-1})+(p_{-1}'f_1)]$. See original paper parameter values.
H. Shull and D. Ebbing, J. Chem. Phys. **28**, 866 (1958)	3.9264 (0.14430)	1.42	$\Psi=1s_c1s_d+1s_d1s_c$ "floating orbitals" (see Gurnee, Magee). $\zeta=1.165$ $x=0.055$.
	3.5814 (0.13162)	1.387	$\Psi=\varphi(1)\varphi(2)$, where $\varphi=1s_c1s_d$, "floating." $\zeta=1.187$, $x=0.045$.
	4.0853 (0.15014)	1.43	$\Psi=1s_c1s_d+1s_d1s_c+[1s_c1s_c+1s_d1s_d]$. $\zeta=1.190$, $x=0.036$. All parameters minimized, integrals computed carefully.
S. Hagstrom[h]	4.7109 (0.17313)	1.4	Configuration interaction in elliptical coordinates, $\Psi=\Sigma c_n\psi_n$. $\psi_{mnj}=[(\xi^2-1)(1-\eta^2)]^{m/2}\xi^n\eta^j\exp(-\alpha\xi-\beta\eta)\exp(im\phi)$. Thirty-four terms up to $m=3$, $\alpha=1.0$, $\beta=0$.

[g] This number must be in error, since an orbital product cannot improve on SCF.
[h] Papers unpublished at time of compilation of bibliography.

Reference	B.E.[a]	R	Details of calculation
	4.3819 (0.16104)	1.4	Same function except all $m=0$ terms, 31 terms.
W. Kolos[h]	4.6955 (0.17257)	1.4	Correlated orbital, closed shell. $\Psi=\varphi(1)\varphi(2)\chi(r_{12})$, $\varphi=\exp(-\alpha\xi)\Sigma_{mn}c_{mn}\xi^m\eta^n$, $\chi=\Sigma_i a_i r_{12}^i$.
	4.7061 (0.17296)	1.4	Correlated orbital, open shell. $\Psi=[\varphi(1)\psi(2)+\psi(1)\varphi(2)]\chi(r_{12})$. ψ and φ differ in expansion coefficient only. $\alpha=0.95$, both cases (α minimized).
W. Kolos[h]	4.7465 (0.17444)	1.4	40-term James and Coolidge type function, $\alpha=0.95$ (minimized). Computes potential curve from $R=0.4$ to 4.2 varying α along curve.
	4.3789	1.4	Twenty-seven term James and Coolidge type function without r_{12} terms, $\alpha=0.95$.
H. Shull and S. Hagstrom, J. Chem. Phys. **30,** 1314 (1959)	4.3920 (0.16141)	1.4	Single-center Laguerre function at center of molecule. $\Psi=\Sigma c_{n,l}\exp(-\eta r)L_{n+l+1}^{2l+2}(2\eta r)Y_l^m(\theta,\varphi)$. 44 configurations up to $7i_0$. $\eta_s R=\eta_p R=\eta_d R=2.9$, $\eta_g R=8.7$, $\eta_i R=11.6$.
	4.1049 (0.15086)	1.4 1.4	Same type, but $3p$ configuration—all orbitals axially symmetric.

Exptl. B.E.=4.746 ev at $R=1.4008$ a.u.=0.74166 A. $\nu_{\text{exptl.}}=4401$ cm^{-1}.[i]

[i] See reference 14.