Accurate Electronic Wave Functions for the H_2 Molecule*

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INTRODUCTION

THE pioneering work of James and Coolidge[1] on the ground state of the hydrogen molecule established beyond a doubt the usefulness of including the interelectronic distance explicitly in the wave function. Subsequent applications of the method to a number of excited states by these authors and Present[2–5] were about equally successful. Wherever experimental energies were known, the agreement between computed and observed values was within 0.02–0.08 ev, the lower figure applying to the ground state.

We considered it important to extend these calculations in accuracy and scope. The ideal goal is to obtain accurate wave functions which correctly describe the electronic, vibrational, and rotational motion of the molecule. The present paper deals with electronic wave functions only. We set ourselves the following tasks: (1) to increase the accuracy of the energy calculations by several significant figures; (2) to perform calculations for many values of the internuclear distance so that accurate potential energy curves could be obtained; (3) to carry out more elaborate calculations of the expectation values of various operators other than the energy; (4) to compare the accurate wave functions obtained with other more approximate wave functions, one of which is the SCF (self-consistent field) function.

This comparison with more approximate wave functions is of particular interest as a basis for understanding the validity and limitations of such functions for more than two-electron systems, where we cannot hope to construct wave functions of the same accuracy as the best H_2 functions. The present calculations should stimulate further work, for instance, on the coupling of the electronic wave function with nuclear moments.

ACCURATE WAVE FUNCTION FOR THE GROUND STATE; EVALUATION OF THE ULATIVE ELEMENTS

For a given internuclear distance R, the accurate wave function for the ground state is expanded in the form[1]

$$\Phi=\sum_i c_i\Phi_i, \tag{1}$$

where

$$\Phi_i=\Psi_{p_iq_ir_is_i\mu_i}+\Psi_{r_is_ip_iq_i\mu_i}, \tag{2}$$

$$\Psi_{pqrs\mu}=e^{-\alpha(\xi_1+\xi_2)}\xi_1{}^p\eta_1{}^q\xi_2{}^r\eta_2{}^s r_{12}{}^\mu. \tag{3}$$

Obviously Φ_i is symmetrical in the indices 1 and 2, so that it represents a singlet. If q_i+s_i is even Φ_i is symmetrical with respect to inversion at the center of the molecule; since there is no azimuthal dependence, this means that Φ_i belongs to the species $^1\Sigma_g{}^+$. The expansion coefficients c_i satisfy

$$\sum_j(H_{ij}-ES_{ij})c_j=0, \tag{4}$$

where

$$H_{ij}=\langle\Phi_i|\,\mathcal{H}\,|\Phi_j\rangle,\quad S_{ij}=\langle\Phi_i|\Phi_j\rangle, \tag{5}$$

and $\mathcal{H}$ is the electronic Hamiltonian. The energy E is the lowest root of

$$\mathrm{Det}(\mathbf{H}-E\mathbf{S})=0. \tag{6}$$

The electronic Hamiltonian is given by

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_2+\mathcal{H}_{12}, \tag{7}$$

where

$$\mathcal{H}_\lambda=-\tfrac{1}{2}\Delta_\lambda-[(r_{a\lambda})^{-1}+(r_{b\lambda})^{-1}],\quad \lambda=1,2, \tag{8}$$
$$\mathcal{H}_{12}=(r_{12})^{-1}.$$

For the evaluation of the matrix elements it is useful to define the unsymmetrical Hamiltonian

$$\mathcal{H}'=2\mathcal{H}_1+\mathcal{H}_{12}; \tag{9}$$

namely, since the Φ_i's are symmetrical in 1, 2 we find, using Eqs. (2), (3), (5),

$$\begin{aligned}H_{ij}=\langle\Phi_i|\,\mathcal{H}\,|\Phi_j\rangle&=\langle\Phi_i|\,\mathcal{H}'\,|\Phi_j\rangle\\&=\langle p_iq_ir_is_i\mu_i|\,\mathcal{H}'\,|p_jq_jr_js_j\mu_j\rangle\\&\quad+\langle p_iq_ir_is_i\mu_i|\,\mathcal{H}'\,|r_js_jp_jq_j\mu_j\rangle\\&\quad+\langle r_is_ip_iq_i\mu_i|\,\mathcal{H}'\,|p_jq_jr_js_j\mu_j\rangle\\&\quad+\langle r_is_ip_iq_i\mu_i|\,\mathcal{H}'\,|r_js_jp_jq_j\mu_j\rangle,\end{aligned} \tag{10}$$

where $\langle pqrs\mu|\,\mathcal{H}'\,|p'q'r's'\mu'\rangle$ is an obvious symbolic abbreviation for $\langle\Psi_{pqrs\mu}|\,\mathcal{H}'\,|\Psi_{p'q'r's'\mu'}\rangle$. The analogous expression for the overlap matrix elements S_{ij} can be obtained from (10) by replacing $\mathcal{H}'$ by the identity operator.

We now proceed to evaluate $\langle pqrs\mu|\,\mathcal{H}'\,|p'q'r's'\mu'\rangle$ and

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[2] R. D. Present, J. Chem. Phys. 3, 122 (1935).
[3] A. S. Coolidge, H. M. James, and R. D. Present, J. Chem. Phys. 4, 193 (1936).
[4] A. S. Coolidge and H. M. James, J. Chem. Phys. 6, 730 (1938).
[5] H. M. James and A. S. Coolidge, Astrophys. J. 87, 438 (1938).

$\langle pqrs\mu|p'q'r's'\mu'\rangle$ in terms of the primitive integrals

$$K_{pqrs}{}^{\mu}=\int\int dV_1dV_2(\xi_1{}^2-\eta_1{}^2)^{-1}e^{-2\alpha(\xi_1+\xi_2)}\times\xi_1{}^p\eta_1{}^q\xi_2{}^r\eta_2{}^s r_{12}{}^{\mu}. \quad (11)$$

First we transform the contribution from the kinetic energy. We write

$$-\langle pqrs\mu|\Delta_1|p'q'r's'\mu'\rangle=\int dV_2\varphi_{rs}(2)\varphi_{r's'}(2)\times\int dV_1[\nabla_1\varphi_{pq}(1)r_{12}{}^{\mu}]\cdot[\nabla_1\varphi_{p'q'}(1)r_{12}{}^{\mu'}], \quad (12)$$

where

$$\varphi_{pq}(\lambda)=e^{-\alpha\xi_\lambda}\xi_\lambda{}^p\eta_\lambda{}^q. \quad (13)$$

The integral over electron 1 in Eq. (12) is transformed as follows:

$$\begin{aligned}\int dV_1\{&[\nabla_1\varphi_{pq}(1)]\cdot[\nabla_1\varphi_{p'q'}(1)]r_{12}{}^{\mu+\mu'}\\&+\varphi_{pq}(1)\varphi_{p'q'}(1)[\nabla_1 r_{12}{}^{\mu}]\cdot[\nabla_1 r_{12}{}^{\mu'}]\\&+[\varphi_{pq}(1)\nabla_1\varphi_{p'q'}(1)]\cdot[r_{12}{}^{\mu'}\nabla_1 r_{12}{}^{\mu}]\\&+[\varphi_{p'q'}(1)\nabla_1\varphi_{pq}(1)]\cdot[r_{12}{}^{\mu}\nabla_1 r_{12}{}^{\mu'}]\}\\=\int dV_1\{&[\nabla_1\varphi_{pq}(1)]\cdot[\nabla_1\varphi_{p'q'}(1)]r_{12}{}^{\mu+\mu'}\\&+\mu\mu'\varphi_{pq}(1)\varphi_{p'q'}(1)r_{12}{}^{\mu+\mu'-2}\\&+(\mu+\mu')^{-1}[\mu\varphi_{pq}(1)\nabla_1\varphi_{p'q'}(1)\\&\qquad+\mu'\varphi_{p'q'}(1)\nabla_1\varphi_{pq}(1)]\cdot[\nabla_1 r_{12}{}^{\mu+\mu'}]\}\\=\int dV_1\{&\mu\mu'\varphi_{pq}(1)\varphi_{p'q'}(1)r_{12}{}^{\mu+\mu'-2}\\&-(\mu+\mu')^{-1}[\mu\varphi_{pq}(1)\Delta_1\varphi_{p'q'}(1)\\&\qquad+\mu'\varphi_{p'q'}(1)\Delta_1\varphi_{pq}(1)]r_{12}{}^{\mu+\mu'}, \quad (14)\end{aligned}$$

where we used Green's theorem. This expression is still valid if either $\mu=0$ or $\mu'=0$; it holds, in addition, for $\mu=\mu'=0$ if we interpret in this case

$$\mu/(\mu+\mu')=\mu'/(\mu+\mu')=\tfrac{1}{2}.$$

The desired expression for the kinetic energy contribution in terms of the primitive integrals (11) is now easily obtained by substituting (14) into Eq. (12), using the well-known expression for Δ_1 in elliptic coordinates, and carrying out the differentiation. The other contributions to $\langle pqrs\mu|\mathcal{H}'|p'q'r's'\mu'\rangle$ are simple and obvious; so is $\langle pqrs\mu|p'q'r's'\mu'\rangle$. The complete results are

$$\begin{aligned}\langle pqrs\mu|\mathcal{H}'|p'q'r's'\mu'\rangle\\=-4R^{-2}\{&\alpha^2(K_{\bar p+2,\bar q\bar r\bar s}{}^{\bar\mu}-K_{\bar p\bar q\bar r\bar s}{}^{\bar\mu})\\&-2\alpha[\tilde p(K_{\bar p+1,\bar q\bar r\bar s}{}^{\bar\mu}-K_{\bar p-1,\bar q\bar r\bar s}{}^{\bar\mu})+2K_{\bar p+1,\bar q\bar r\bar s}{}^{\bar\mu}]\\&+[\tilde p(\bar p+1)-pp'](K_{\bar p\bar q\bar r\bar s}{}^{\bar\mu}-K_{\bar p-2,\bar q\bar r\bar s}{}^{\bar\mu})\\&-[\tilde q(\bar q+1)-qq'](K_{\bar p\bar q\bar r\bar s}{}^{\bar\mu}-K_{\bar p,\bar q-2,\bar r\bar s}{}^{\bar\mu})\\&+2\tilde pK_{\bar p-2,\bar q\bar r\bar s}{}^{\bar\mu}-2\tilde qK_{\bar p,\bar q-2,\bar r\bar s}{}^{\bar\mu}\}\\&+\mu\mu'(K_{\bar p+2,\bar q\bar r\bar s}{}^{\bar\mu-2}-K_{\bar p,\bar q+2,\bar r\bar s}{}^{\bar\mu-2})\\&\quad-8R^{-1}K_{\bar p+1,\bar q\bar r\bar s}{}^{\bar\mu}+K_{\bar p+2,\bar q\bar r\bar s}{}^{\bar\mu-1}-K_{\bar p,\bar q+2,\bar r\bar s}{}^{\bar\mu-1},\\\langle pqrs\mu|p'q'r's'\mu'\rangle&=K_{\bar p+2,\bar q\bar r\bar s}{}^{\bar\mu}-K_{\bar p,\bar q+2,\bar r\bar s}{}^{\bar\mu}, \quad (15)\end{aligned}$$

with

$$\bar\mu=\mu+\mu',\quad \bar p=p+p',\quad \tilde p=(\mu'p+\mu p')/\bar\mu, \quad (16)$$

and $\bar q$, $\bar r$, $\bar s$, $\tilde q$, $\tilde r$, $\tilde s$ defined analogous to $\bar p$ and $\tilde p$. The evaluation of the primitive integrals $K_{pqrs}{}^{\mu}$ in terms of standard functions was given in a preceding paper[6] for $-1\leqslant\mu\leqslant4$, which is necessary and sufficient for wave functions which contain terms with r_{12} and $r_{12}{}^2$.

ACCURATE WAVE FUNCTIONS FOR EXCITED STATES

The lower electronic excited states can be treated in the same fashion as the ground state. The states we treated were:

(1) The repulsive $^3\Sigma_u{}^+$ state, which dissociates into normal atoms. The wave function is in this case represented by

$$\Phi_i=\Psi_{p_iq_ir_is_i\mu_i}-\Psi_{r_is_ip_iq_i\mu_i},$$

where q_i+s_i is odd, and $\Psi_{pqrs\mu}$ is given by Eq. (3). The expression for the matrix elements $\langle\Phi_i|\mathcal{H}|\Phi_j\rangle$ and $\langle\Phi_i|\Phi_j\rangle$ is a rather obvious modification of Eq. (10). Since this state is the lowest of its species, the energy is again the lowest root of the appropriate secular equation.

(2) The attractive $^1\Sigma_u{}^+$ state, which dissociates into $1s$ and $(2s, 2p\sigma)$ atoms. For the wave function Φ_i Eq. (2) holds, but now q_i+s_i is odd. Again, the energy is the lowest root of the secular equation.

(3) The first excited (attractive) $^1\Sigma_g{}^+$ state, which dissociates into a proton and the ground state of H^-. The wave function is of the same form as for the ground state, but the energy is the next to the lowest root of the secular equation. When carrying out the calculation there is no need to keep the wave function orthogonal to the ground state function; it is sufficient to always pick the next lowest root in the secular equation at every stage of approximation, which guarantees that this energy is always an upper bound to the actual energy.[7]

[6] W. Kolos and C. C. J. Roothaan, Revs. Modern Phys. **32**, 205 (1960), this issue.
[7] P. O. Löwdin (private communication).

APPROXIMATE WAVE FUNCTIONS FOR THE GROUND STATE

For more than two-electron systems, accurate calculations are far more difficult than for H_2. In particular, it seems at present rather impossible to include the interelectronic distances explicitly in the wave functions for more than two electrons, or certainly for more than three or four. In order to gain some insight into the reliability of more approximate wave functions for n-electron systems, it is useful to carry out such calculations on H_2 and compare the results with the accurate ones.

An approximate function of great interest for n-electron systems in the SCF function. The SCF function for H_2 was first determined by Coulson,[8] who used a five-term expansion in elliptic coordinates for the orbital. In a preceding paper[6] we reported a slightly improved orbital using the same terms as Coulson's but minimizing also for the exponent α. In conjunction with the present work we decided to increase the flexibility of the orbital by increasing the number of terms. The orbital is expanded according to

$$\varphi=\sum_i a_i\varphi_i, \tag{17}$$

where the basis functions φ_i are defined by

$$\varphi_i=e^{-\alpha\xi}\xi^{p_i}\eta^{q_i}, \tag{18}$$

and q_i is always even since all functions φ_i are of species σ_g. The orbital (17) is normalized, hence

$$\sum_{ij} a_iS_{ij}a_j=1, \tag{19}$$

where

$$S_{ij}=\langle\varphi_i|\,\varphi_j\rangle. \tag{20}$$

The orbital coefficients satisfy the pseudoeigenvalue problem

$$\sum_j (F_{ij}-\epsilon S_{ij})a_j=0, \tag{21}$$

where

$$F_{ij}=H_{ij}+\sum_{kl} \mathcal{J}_{ijkl}a_ka_l, \tag{22}$$

$$H_{ij}=\langle\varphi_i|\,-\tfrac{1}{2}\Delta-(r_a)^{-1}-(r_b)^{-1}|\,\varphi_j\rangle,$$

$$\mathcal{J}_{ijkl}=\int\int dV_1dV_2\varphi_i(1)\varphi_j(1)\varphi_k(2)\varphi_l(2)r_{12}^{-1}. \tag{23}$$

The orbital energy ϵ is the lowest root of the secular equation

$$\mathrm{Det}(\mathbf{F}-\epsilon\mathbf{S})=0; \tag{24}$$

the total electronic energy is given by

$$E=\sum_{ij} a_i(H_{ij}+F_{ij})a_j. \tag{25}$$

[8] C. A. Coulson, Proc. Cambridge Phil. Soc. **34**, 204 (1938).

The evaluation of the matrix elements S_{ij}, H_{ij} and of the supermatrix elements $\mathcal{J}_{ijkl}$ is elementary and straightforward; the kinetic energy part of H_{ij} is first transformed into $\frac{1}{2}\int dV(\nabla\varphi_i)\cdot(\nabla\varphi_j)$ using Green's theorem. The integrated expressions for the various quantities are

$$\begin{aligned} H_{ij}=\pi R\{&(q+1)^{-1}[\alpha^2A_p(2\alpha)-\alpha pA_{p-1}(2\alpha)\\ &+p_ip_jA_{p-2}(2\alpha)]+(q-1)^{-1}q_iq_jA_p(2\alpha)\}\\ &-2\pi R^2(q+1)^{-1}A_{p+1}(2\alpha), \end{aligned} \tag{26}$$

$$S_{ij}=\tfrac{1}{2}\pi R^3[(q+1)^{-1}A_{p+2}(2\alpha)-(q+3)^{-1}A_p(2\alpha)],$$

$$\mathcal{J}_{ijkl}=K_{p+2,q\bar{p}\bar{q}}{}^{-1}-K_{p,q+2,\bar{p}\bar{q}}{}^{-1},$$

where we have used the abbreviations

$$\begin{aligned} p&=p_i+p_j, & q&=q_i+q_j,\\ \bar{p}&=p_k+p_l, & \bar{q}&=q_k+q_l. \end{aligned} \tag{27}$$

The primitive integrals $K_{pqrs}{}^{-1}$ are given by Eq. (11), and $A_n(x)$ is given in a preceding paper,[6] Eq. (26). The SCF calculation is performed by iteration, using each time the coefficients a_i which solve Eq. (21) to calculate the SCF Hamiltonian F_{ij} according to Eq. (22) for the next approximation. The usual exchange contribution is absent in Eq. (22); this is possible in this special case of two paired electrons forming a singlet ground state.

Another important form of wave function is a superposition of configurations. Equations (1)–(3) define such a superposition if $\mu=0$. For the ground state q_i+s_i must be even; the terms with q_i and s_i even represent configurations of the type $\sigma_g\sigma_g'$, those with q_i and s_i odd configurations of the type $\sigma_u\sigma_u'$. Obviously the set thus obtained is not sufficiently general; however, configurations of the types $\pi_g\pi_g'$ or $\pi_u\pi_u'$, $\delta_g\delta_g'$ or $\delta_u\delta_u'$, etc. can easily be constructed from this set by multiplying the appropriate terms with $\cos(\varphi_1-\varphi_2)$, $\cos2(\varphi_1-\varphi_2)$, etc.

EXPECTATION VALUES OF VARIOUS OPERATORS FOR THE GROUND STATE

To judge the quality of an approximate wave function, the criterion of how close the calculated energy agrees with the experimental one is often only a crude measure. This is due to the fact that the root-mean-square error in the wave function is roughly equal to the square root of the relative error in the energy; hence if the energy is accurate to, say four significant figures, we expect the wave function to be accurate to about two significant figures. The latter is furthermore an *average* of that error integrated over the coordinates of all the electrons; it is quite conceivable, and actually almost always true in practice, that for certain critical values of the electron coordinates the error in the wave function is considerably larger, and sometimes infinite. If expectation values of certain operators are evaluated with the approximate wave functions, different operators may weigh these critical points quite differently, and it is therefore quite possible that wave functions

TABLE I. Binding energies (in ev) for the ground state of H_2 computed with 3- to 15-term wave functions and different exponents ($R=1.4$).

No. of terms	ξ_1	η_1	ξ_2	η_2	r_{12}	$\alpha=0.75$	$\alpha=0.875$	$\alpha=0.95$
1	0	0	0	0	0			
2	0	0	0	2	0			
3	0	0	1	0	0	3.5960		3.6416
4	0	1	0	1	0	4.0814		4.1263
5	0	0	0	0	1	4.5297	4.6464	4.6698
6	1	1	0	1	0	4.5823	4.6562	4.6705
7	1	0	0	2	0	4.5967	4.6562	4.6753
8	0	0	2	0	0	4.6132	4.6602	4.6912
9	0	0	0	0	2	4.6931	4.7048	4.7098
10	0	1	0	1	1	4.6932	4.7050	4.7098
11	0	0	1	2	0	4.7073	4.7057	4.7104
12	0	0	0	2	1	4.7146	4.7149	4.7183
13	0	0	1	0	1	4.7220	4.7265	4.7225
14	1	0	1	0	0	4.7226	4.7397	4.7406
15	1	1	1	1	0	4.7262	4.7408	4.7415

which yield good energies yield poor values for the exptation values of other operators.

In order to gain some insight into these matters by purely theoretical means, one can proceed as follows. First we calculate the expectation values of an operator with various wave functions of the accurate form, increasing the flexibility of the wave function by increasing the length of the expansion. Inspection of these calculated expectation values as a function of the expansion length then enables us to judge to how many figures these expectation values have converged for the best accurate wave function; these results are then adopted as the "experimental" values for these quantities. The expectation values calculated with various other approximate wave functions (e.g., SCF) can then be compared with these experimental values.

This procedure may seem somewhat awkward, since one would really want to compare calculated values with actual experimental values obtained from spectroscopic, thermodynamic, etc. measurements. The difficulty is, however, that we have so far obtained only an *electronic* wave function, and the results of actual measurements strictly can be compared only with values calculated from a wave function describing the electronic, vibrational, and rotational motion. In addition, our electronic wave functions are calculated

TABLE II. Energies and expectation values of r_{12}^{-1} and ξ for the ground state of H_2 computed with 4- to 40-term wave functions ($\alpha=0.95$, $R=1.4$).

No. of terms	ξ_1	η_1	ξ_2	η_2	r_{12}	$-E$(a.u.)	D(ev)	$V/2E$	$\langle r_{12}^{-1}\rangle$	$\langle\xi\rangle$
1	0	0	0	0	0					
2	0	0	0	2	0					
3	0	0	1	0	0					
4	0	1	0	1	0	1.151645	4.1262	1.00628	0.62942	2.1825
5	0	0	0	0	1	1.171619	4.6697	1.00056	0.59380	2.1917
6	1	1	0	1	0	1.171645	4.6704	1.00106	0.59405	2.1909
7	1	0	0	2	0	1.171823	4.6753	0.99984	0.59332	2.1933
8	0	0	2	0	0	1.172407	4.6912	0.99612	0.58928	2.2153
9	0	0	0	0	2	1.173091	4.7098	0.99913	0.59012	2.2092
10	0	1	0	1	1	1.173091	4.7098	0.99909	0.59012	2.2093
11	0	0	1	2	0	1.173112	4.7103	0.99920	0.58998	2.2095
12	0	0	0	2	1	1.173402	4.7182	0.99946	0.58961	2.2092
13	0	0	1	0	1	1.173559	4.7225	1.00051	0.58935	2.2083
14	1	0	1	0	0	1.174224	4.7406	1.00029	0.58768	2.2111
15	1	1	1	1	0	1.174257	4.7415	1.00030	0.58767	2.2111
16	0	0	1	0	2	1.174269	4.7418	1.00032	0.58766	2.2116
17	0	2	0	2	0	1.174305	4.7428	1.00040	0.58767	2.2116
18	0	1	0	1	2	1.174308	4.7429	1.00040	0.58767	2.2115
19	1	0	2	0	1	1.174314	4.7430	1.00036	0.58762	2.2118
20	0	0	2	0	1	1.174316	4.7431	1.00041	0.58766	2.2114
21	1	1	1	1	2	1.174333	4.7436	1.00043	0.58766	2.2113
22	0	0	2	0	2	1.174335	4.7436	1.00043	0.58765	2.2114
23	1	0	0	2	1	1.174338	4.7437	1.00039	0.58762	2.2116
24	1	1	1	1	1	1.174348	4.7440	1.00038	0.58761	2.2116
25	1	0	1	0	1	1.174357	4.7442	1.00033	0.58758	2.2118
26	0	0	0	2	2	1.174357	4.7442	1.00033	0.58757	2.2118
27	1	0	2	0	0	1.174359	4.7443	1.00030	0.58756	2.2119
28	1	0	0	2	2	1.174360	4.7443	1.00030	0.58756	2.2119
29	1	2	3	0	0	1.174365	4.7444	1.00029	0.58755	2.2119
30	2	0	3	0	0	1.174375	4.7447	1.00027	0.58752	2.2121
31	1	0	1	0	2	1.174377	4.7448	1.00026	0.58751	2.2121
32	0	0	3	0	0	1.174413	4.7457	1.00016	0.58745	2.2123
33	1	0	1	2	0	1.174430	4.7462	1.00017	0.58739	2.2126
34	0	1	2	1	0	1.174432	4.7463	1.00018	0.58739	2.2126
35	1	0	3	0	0	1.174433	4.7463	1.00017	0.58739	2.2125
36	1	2	1	2	0	1.174433	4.7463	1.00018	0.58739	2.2126
37	1	1	2	1	0	1.174434	4.7463	1.00017	0.58739	2.2126
38	0	2	3	0	0	1.174440	4.7465	1.00017	0.58737	2.2127
39	3	0	3	0	0	1.174440	4.7465	1.00017	0.58737	2.2127
40	2	1	2	1	0	1.174440	4.7465	1.00017	0.58737	2.2127

TABLE III. Energies and expectation values of r^2 and $3z^2-r^2$ for the ground state of H_2 computed with 4- to 28-term wave functions ($\alpha=0.95$, $R=1.4$).

No. of terms	ξ_1	η_1	ξ_2	η_2	r_{12}	$-E$(a.u.)	D(ev)	$V/2E$	$\langle r^2\rangle$	$\langle 3z^2-r^2\rangle$
1	0	0	0	0	0					
2	0	0	0	2	0					
3	0	0	1	0	0					
4	0	1	0	1	0	1.151645	4.1262	1.00628	2.4290	0.5148
5	0	0	0	0	1	1.171619	4.6697	1.00056	2.4609	0.4823
6	1	1	0	1	0	1.171645	4.6704	1.00106	2.4587	0.4803
7	1	0	0	2	0	1.171823	4.6753	0.99984	2.4653	0.4822
8	0	0	2	0	0	1.172407	4.6912	0.99612	2.5456	0.4855
9	0	0	0	0	2	1.173091	4.7098	0.99913	2.5276	0.4835
10	1	0	1	0	0	1.173943	4.7329	1.00087	2.5334	0.4860
11	0	2	0	2	0	1.173970	4.7337	1.00104	2.5327	0.4868
12	0	0	0	2	1	1.174191	4.7397	1.00085	2.5347	0.5227
13	0	0	1	0	1	1.174254	4.7414	1.00018	2.5382	0.5221
14	1	1	1	1	0	1.174282	4.7422	1.00021	2.5381	0.5215
15	0	0	1	0	2	1.174296	4.7426	1.00023	2.5412	0.5224
16	1	0	2	0	0	1.174307	4.7429	1.00014	2.5433	0.5230
17	0	1	0	1	1	1.174313	4.7430	1.00021	2.5432	0.5199
18	0	1	0	1	2	1.174314	4.7430	1.00022	2.5428	0.5205
19	1	0	2	0	1	1.174314	4.7430	1.00022	2.5429	0.5202
20	0	0	2	0	1	1.174317	4.7431	1.00027	2.5408	0.5201
21	1	1	1	1	2	1.174336	4.7436	1.00034	2.5404	0.5159
22	0	0	2	0	2	1.174338	4.7437	1.00033	2.5408	0.5157
23	1	0	0	2	1	1.174341	4.7438	1.00032	2.5414	0.5148
24	1	1	1	1	1	1.174350	4.7440	1.00036	2.5412	0.5138
25	1	0	1	0	1	1.174358	4.7442	1.00034	2.5423	0.5135
26	0	0	0	2	2	1.174358	4.7442	1.00033	2.5423	0.5145
27	1	0	1	0	2	1.174359	4.7443	1.00033	2.5424	0.5145
28	1	0	0	2	2	1.174360	4.7443	1.00033	2.5426	0.5142

neglecting certain other smaller effects, like relativistic corrections, coupling with nuclear moments, etc. The true experimental values *do* contain all these effects. As a result, even if we had obtained calculated values for operators with an electronic-vibrational-rotational wave function, comparison with experiment would still leave some uncertainty as to whether a discrepancy was due to the approximate nature of the wave function as a solution of the actual Hamiltonian used or to the neglect of certain small terms in the Hamiltonian.

The operators we investigated were r_{12}^{-1}, ξ_1, r_1^2, and $3z_1^2-r_1^2$. The first two are not directly comparable to experimental data, but give some idea about the wave function: r_{12}^{-1} is the total electronic repulsion energy; and $\xi=\langle\xi_1\rangle$ is an ellipsoid with the protons as foci, which is a measure for the size of the molecular charge cloud. The other two operators do have a direct relation to experiment, namely, the Larmor term in the molar diamagnetic susceptibility is given by[9]

$$\chi_L=\tfrac{1}{6}Nr_0a_0^2\sum_{\lambda=1}^{2}\langle r_\lambda^2\rangle; \tag{28}$$

N is Avogadro's number, $r_0=e^2/mc^2$ is the classical electron radius, and $a_0=\hbar^2/me^2$ is the Bohr radius for infinite nuclear mass. For the evaluation of $\langle r_\lambda^2\rangle$, lengths are measured in Bohr radii. The operator $3z_1^2-r_1^2$ is related to the molecular quadrupole moment, which is given by

$$Q=ea_0^2(R^2-\sum_{\lambda=1}^{2}\langle 3z_\lambda^2-r_\lambda^2\rangle); \tag{29}$$

the term $ea_0^2R^2$ represents the contribution of the nuclei. In Eqs. (28) and (29) the contributions from the two electrons are the same. By using the most recent values for the physical constants,[10] we obtain for the last two formulas in cgs units

$$\chi_L=1.5847\times10^{-6}\langle r_1^2\rangle, \tag{30}$$

$$Q=1.3449\times10^{-26}(R^2-2\langle 3z_1^2-r_1^2\rangle). \tag{31}$$

The actual evaluation of $\langle r_{12}^{-1}\rangle$, $\langle\xi_1\rangle$, $\langle r_1^2\rangle$ and $\langle 3z_1^2-r_1^2\rangle$ in terms of primitive integrals is straightforward, and we omit the explicit formulas.

RESULTS AND DISCUSSION

The computations were carried out on the Remington Rand Univac Scientific 1103 and 1103A computers at Wright-Patterson Air Force Base. The first set of computations was a slight extension of the first calculations by James and Coolidge.[1] The binding energy was computed for $R=1.4$, which is close to the equilibrium distance, for various values of α and expansions of up to 15 terms. The results are shown in Table I; the energies on a horizontal line in this table apply to a wave function containing the terms in the second

[9] J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, New York, 1932).

[10] E. R. Cohen and J. W. DuMond, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 35, p. 82.

column *on* and *above* that horizontal line. These computations served as a mutual check between our results and those of James and Coolidge,[1] and also to determine the best value of α. This best value is dependent on the expansion used but appears to converge for longer expansions (although the value of α would be immaterial for infinite expansion length). Curiously, for the 11-term expansion there are two minima in the energy at about $\alpha=0.75$ and $\alpha=0.95$, the latter giving a slightly lower energy than the former. It was just this case from which James and Coolidge determined $\alpha=0.75$; clearly $\alpha=0.95$ is a better choice, since that minimum is lower and persists for the longer expansions.

Having roughly optimized $\alpha=0.95$ for the equilib-

TABLE IV. Total and potential energies (negative values) for the ground state of H_2 computed with 40-term wave functions.

						Interpolated values			
$R\diagdown\alpha$	0.55	0.75	0.95	1.15		$-E$(a.u.)	D(ev)	$V/2E$	α
0.4	0.116159	0.070477							
	2.393350	2.581826							
0.6	0.769577	0.767817							
	2.677134	2.692277							
0.8	1.019976	1.020012	1.018605			1.020175	0.5490	1.306482	0.6550
	2.666502	2.667387	2.668597						
0.9	1.083543	1.083627	1.083239			1.083651	2.2761	1.219026	0.6856
	2.623531	2.623881	2.627796						
1.0	1.124410	1.124517	1.124428			1.124517	3.3881	1.143352	0.7592
	2.570838	2.571394	2.572728						
1.1	1.149855	1.150023	1.150021			1.150043	4.0826	1.093637	0.8477
	2.513719	2.515112	2.515591						
1.2	1.164576	1.164889	1.164913	1.164716		1.164930	4.4877	1.055048	0.8715
	2.455134	2.458174	2.458405	2.460316					
1.3		1.172286	1.172322	1.172250		1.172323	4.6889	1.024703	0.9170
		2.402416	2.402648	2.403511					
1.35		1.173891	1.173934	1.173894		1.173934	4.7327	1.011824	0.9538
		2.375324	2.375621	2.376217					
1.39		1.174369	1.174419	1.174396		1.174420	4.7459	1.002439	0.9871
		2.354108	2.354489	2.354942					
1.40		1.174388	1.174440	1.174421		1.174442	4.7465	1.000209	0.9958
		2.348867	2.349278	2.349703					
1.41		1.174370	1.174425	1.174409		1.174428	4.7461	1.998022	1.0040
		2.343657	2.344097	2.344497					
1.45		1.173950	1.174015	1.174010		1.174022	4.7351	0.989695	1.0340
		2.323101	2.323677	2.323997					
$R\diagdown\alpha$	0.95	1.15	1.35	1.55	1.75				
1.5	1.172806	1.172810	1.172650			1.172828	4.7026	0.979056	1.0549
	2.298863	2.299122	2.300458						
1.6	1.168515	1.168533	1.168454	1.168003		1.168538	4.5859	0.963510	1.0863
	2.251699	2.251923	2.252680	2.255676					
1.8	1.154937	1.154982	1.154972	1.154814		1.154985	4.2171	0.938545	1.2138
	2.167467	2.167888	2.168247	2.169401					
2.0	1.137869	1.137973	1.137997	1.137946		1.137999	3.7549	0.921651	1.3140
	2.096283	2.097403	2.097758	2.098364					
2.2		1.119844	1.119903	1.119909	1.119800	1.119920	3.2630	0.910970	1.4589
		2.039589	2.040184	2.040715	2.041631				
2.4		1.101912	1.102032	1.102083	1.102058	1.102084	2.7777	0.905188	1.5838
		1.993156	1.994388	1.995065	1.995865				
$R\diagdown\alpha$	1.55	1.75	1.95	2.15	2.55				
2.6	1.085245	1.085288	1.085218			1.085288	2.3207	0.903420	1.7257
	1.960110	1.961067	1.962183						
2.8		1.069925	1.069947	1.069822		1.069956	1.9035	0.904991	1.8798
		1.935775	1.937076	1.938538					
3.0		1.056171	1.056286	1.056276		1.056297	1.5318	0.909253	2.0338
		1.918449	1.920176	1.921833					
3.2		1.044065	1.044291	1.044395	1.044076	1.044395	1.2080	0.915342	2.1535
		1.907392	1.909784	1.911918	1.916549				
$R\diagdown\alpha$	1.95	2.15	2.55	2.95					
3.6	1.024975	1.025365	1.025649	1.025047		1.025663	0.6983	0.931231	2.4781
	1.901333	1.905194	1.911327	1.916993					
3.8	1.017316	1.017895	1.018482	1.018281		1.018506	0.5035	0.939760	2.6481
	1.899753	1.904895	1.912639	1.918837					
4.0		1.011510	1.012471	1.012606		1.012653	0.3443	0.947843	2.8154
		1.904624	1.914627	1.921749					
4.2		1.005981	1.007388	1.007867		1.007867	0.2141	0.954844	2.9566
		1.903245	1.915874	1.924605					

TABLE V. Variation of R close to R_e for the ground state of H_2 with 40- and 50-term functions, $\alpha=0.995$.

No. of terms	R(a.u.)	$-E$(a.u.)	D(ev)	$-V$	$V/2E$
40	1.3809	1.174369	4.7445	2.359300	1.004497
	1.3909	1.174426	4.7461	2.354061	1.002218
	1.3959	1.174440	4.7465	2.351452	1.001095
	1.3999	1.174444	4.7466	2.349371	1.000206
	1.4009	1.174444	4.7466	2.348852	0.999984
	1.4019	1.174444	4.7466	2.348332	0.999763
	1.4059	1.174440	4.7465	2.346258	0.998884
	1.4109	1.174426	4.7461	2.343672	0.997795
	1.4209	1.174371	4.7446	2.338523	0.995649
50	1.3999	1.174448	4.7467	2.349370	1.000202
	1.4009	1.174448	4.7467	2.348851	0.999981
	1.4019	1.174448	4.7467	2.348331	0.999760

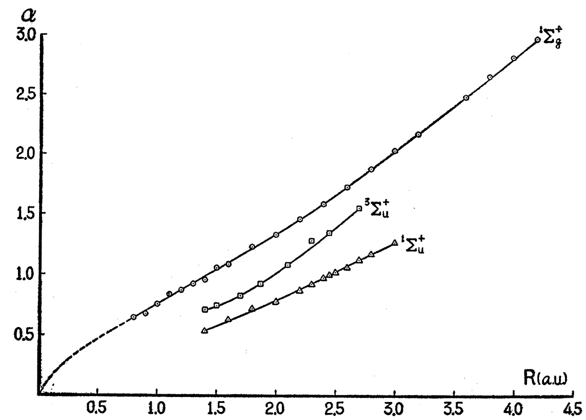

FIG. 1. The optimum exponent α as a function of R for the $^1\Sigma_g{}^+$ ground state and the $^3\Sigma_u{}^+$ and $^1\Sigma_u{}^+$ excited states of H_2.

rium distance, we now kept α fixed at this value and gradually increased the expansion length to 40 terms. The order in which new terms are added to the wave function permits a very large number of paths along which the same 40-term wave function can be reached. Our path is therefore somewhat arbitrary; we exercised some judgment, however, by rejecting terms which did not improve the total energy in the eighth figure. The results are shown in Table II, in which we listed, in addition to the total energy E and the binding energy D, the expectation values $\langle r_{12}^{-1}\rangle$ and $\langle \xi_1\rangle$, and also the ratio $V/2E$, where V is the potential energy (E and V both contain the nuclear repulsion). For any value of R this ratio satisfies

$$V/2E=1+\tfrac{1}{2}(R/E)(dE/dR), \tag{32}$$

which is a consequence of the virial theorem.[11] Incidentally, Eq. (32) also holds if V and E are taken as electronic energies only, omitting the nuclear repulsion from both. From Eq. (32) we see that $V/2E$ should become unity if R is the equilibrium distance; this is true for the exact electronic wave function. The limiting value 1.00017 for this rate at $R=1.4$ indicates that the equilibrium distance is slightly larger than 1.4. Table II shows that $\langle r_{12}^{-1}\rangle$ and $\langle \xi_1\rangle$ have converged to 4–5 significant figures for the 40-term wave function, while the total energy has converged to 6–7 figures and the binding energy to 4–5.

More important than $\langle r_{12}^{-1}\rangle$ and $\langle \xi_1\rangle$ are the expectation values $\langle r_1^2\rangle$ and $\langle 3z_1^2-r_1^2\rangle$. The latter, however, could not be computed for the 40-term function without first computing more primitive integrals. We did the best we could with the available integrals; this necessitated eliminating 12 terms from the 40-term set, which, however, raised the energy only by 0.002 ev. Table III shows that for the 28-term function $\langle r_1^2\rangle$ and $\langle 3z_2^2-r_1^2\rangle$ have converged to 3–4 and 2–3 significant figures, respectively.

The next computation was aimed at obtaining an accurate potential energy curve for the ground state. For each of 27 values of R in the range 0.4–4.2 a calculation was carried out with the same 40 terms as in the previous calculation but reopening the variation of α. The computed values of E and V are contained in the second through the sixth columns of Table IV. For each value of R the best α was then determined by interpolation, minimizing E under the assumption that E versus α is a parabola. This assumption is not quite correct; namely, in those cases where we had four points for a given R, the best α turns out differently depending on which three points are used for the interpolation. This ambiguity, however, hardly affects the minimum value of E, since E versus α is very shallow near that minimum. The interpolated values for E, D, $V/2E$, and α are listed in the seventh through the tenth columns. The validity of the interpolation procedure is further confirmed by Fig. 1, where we plotted the interpolated optimum values of α against R; evidently they lie on a smooth curve.

In order to obtain accurate theoretical values for the binding energy D_e and the equilibrium internuclear distance R_e, we computed more points of the potential energy curve densely spaced around $R=1.4$, with the 40-term function and $\alpha=0.995$, the best value at that distance; this was then repeated for just 3 points with a 50-term function. The resulting values of E, D, V, and $V/2E$ are tabulated in Table V. The computed values of D_e, 4.7466 and 4.7467 ev for the 40- and 50-term functions, respectively, are in excellent agreement with the experimental value[12] 4.7466±0.0007 ev. The most accurate determination of R_e is obtained by invoking the condition $V/2E=1$; we find by this criterion

$$R_e=1.40083 \text{ a.u.}=0.74128 \text{ A}$$

and

$$R_e=1.40081 \text{ a.u.}=0.74127 \text{ A}$$

for the 40- and 50-term functions, respectively. The

[11] J. C. Slater, J. Chem. Phys. 1, 687 (1933).

[12] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

TABLE VI. Normalized wave functions for the ground state of H_2.

No. of terms					5	12	24	40	50
Total energy (a.u.)					−1.171619	−1.174191	−1.174329	−1.174444	−1.174448
Binding energy (ev)					4.6697	4.7397	4.7435	4.7466	4.7467
R(a.u.)					1.4	1.4	1.4	1.4009	1.4009
α					0.95	0.95	0.95	0.995	0.995
ξ_1	η_1	ξ_2	η_2	r_{12}			Coefficients		
0	0	0	0	0	2.144423	2.192089	2.016368	2.077318	2.065908
0	0	0	2	0	1.683396	1.098975	1.010767	1.141281	1.282036
0	0	1	0	0	−0.064683	−0.139338	0.042082	0.137330	0.144619
0	1	0	1	0	−0.513879	−0.377500	−0.301973	−0.422304	−0.430253
0	0	0	0	1	0.815868	0.859247	0.987970	0.835795	0.787198
1	1	0	1	0		−0.058316	−0.360711	−0.246455	−0.235454
1	0	0	2	0		0.078257	0.154088	0.205304	0.148273
0	0	2	0	0		0.150633	0.108738	0.105701	0.109859
0	0	0	0	2		−0.052156		−0.217363	−0.212159
1	0	1	0	0		−0.126629	−0.084347	−0.086291	−0.081387
0	2	0	2	0		0.132561	0.275836	0.196963	0.182892
0	0	0	2	1		0.248411	0.224562	0.203037	0.198555
0	0	1	0	1			−0.249321	0.259626	0.324658
1	1	1	1	0			0.024821	−0.041260	−0.010794
0	0	1	0	2				−0.079797	0.077830
1	0	2	0	0			−0.036452	−0.049768	−0.055114
0	1	0	1	1			0.237109	0.173868	0.130714
0	1	0	1	2				−0.056570	−0.050854
1	0	2	0	1			−0.005136	0.008895	0.014963
0	0	2	0	1			−0.019956	−0.103278	−0.132980
1	1	1	1	2				−0.001197	0.000362
0	0	2	0	2				0.002553	0.006992
1	0	0	2	1			−0.026238	−0.072222	−0.050940
1	1	1	1	1			−0.004118	0.027074	0.018027
1	0	1	0	1			0.082550	0.023814	0.017554
0	0	0	2	2				0.057081	−0.014601
1	0	1	0	2				−0.011466	−0.015172
1	0	0	2	2				0.005322	0.012656
1	2	3	0	0				−0.000293	−0.000202
2	0	3	0	0				−0.001157	−0.000856
0	0	1	2	0			0.091499	0.095599	−0.009469
0	0	3	0	0			0.026725	0.035829	0.036963
1	0	1	2	0			−0.033981	−0.020202	−0.022325
0	1	2	1	0				0.047649	0.053233
1	0	3	0	0				0.005164	0.004690
1	2	1	2	0				0.001963	0.004707
1	1	2	1	0				−0.008791	−0.017531
0	2	3	0	0			0.004723	0.011140	0.017270
3	0	3	0	0				0.000103	0.000082
2	1	2	1	0				−0.000908	0.000031
0	0	1	2	1					0.094436
0	0	3	0	1					0.001789
0	0	3	0	2					−0.000394
0	0	1	2	2					−0.004475
2	0	3	0	1					−0.000121
1	0	1	2	1					−0.014893
2	0	3	0	2					0.000011
1	0	1	2	2					0.001016
0	2	3	0	1					−0.003443
0	2	3	0	2					0.000225

most recent experimental value[13] of 0.74116 A appears to be in disagreement with the computed result. However, this experimental value was obtained from a spectroscopic analysis plus theoretically computed corrections; we expect that a more careful calculation of these corrections would improve the agreement.

Our computer program yielded, besides energies, also the coefficients of the normalized wave functions. To present all the wave functions we obtained is obviously impractical; a selected set, including our best 40- and 50-term functions, is given in Table VI.

For the three excited states mentioned previously, ${}^3\Sigma_u{}^+$, ${}^1\Sigma_u{}^+$, and ${}^1\Sigma_g{}^+$, we carried out calculations with 34, 34, and 40 terms, respectively, for different R values, varying again α for each R value. The results are given in Tables VII–IX; the interpolated α values for the ${}^3\Sigma_u{}^+$ and ${}^1\Sigma_u{}^+$ states are also plotted in Fig. 1. For the excited ${}^1\Sigma_g{}^+$ state we computed only for two α values so that quadratic interpolation was not possible; time did not permit us to complete the necessary computations for this case. The equilibrium distances and energies for the two attractive excited states ${}^1\Sigma_u{}^+$ and ${}^1\Sigma_g{}^+$, as obtained by interpolation from Tables VIII and

[13] G. Herzberg and L. L. Howe, Can. J. Phys. 37, 636 (1959).

TABLE VII. Total and potential energies (negative values) for the lowest $^3\Sigma_u{}^+$ state of H_2 computed with 34-term wave functions.

$R\diagdown\alpha$	0.75	0.95	1.15	Interpolated values $-E$(a.u.)	$1+E$(ev)	$V/2E$	
1.1	0.663466 1.952795						
1.3	0.751875 1.951418						
1.4	0.783024 1.961382	0.778108 1.998449	0.766040 2.057146	0.783150	5.9004	1.249340	0.7125
1.5	0.808950 1.975638	0.806599 1.999232	0.799400 2.043679	0.808950	5.1984	1.221238	0.7530
1.7	0.850323 2.006261	0.850091 2.014488	0.847984 2.035155	0.850456	4.0693	1.180484	0.8253
1.8684	0.877538 2.025708	0.877884 2.031174	0.877338 2.039893	0.877889	3.2226	1.156410	0.9276
2.1	0.906515 2.037345	0.907519 2.046870	0.907619 2.050112	0.907687	2.5118	1.129022	1.0722
$R\diagdown\alpha$	0.75	1.15	1.55				
2.3	0.925075 2.032877	0.927381 2.054490	0.926943 2.063516	0.927540	1.9716	1.109912	1.2862
2.4429	0.935167 2.021892	0.938718 2.053826	0.938729 2.059461	0.938979	1.6604	1.094240	1.3521
2.7	0.947455 1.987367	0.954390 2.0453540	0.954880 2.051367	0.954880	1.2277	1.074142	1.5492
$R\diagdown\alpha$	1.55	1.95					
2.9	0.964039 2.043047	0.964019 2.047858					
3.1	0.970907 2.032939	0.971168 2.037439					
3.3	0.975924 2.021357	0.976457 2.027329					
3.5		0.980302 2.017141					

and IX, as well as those obtained for the ground state, are compared with experimental data in Table X. The agreement for the two excited states is notably poorer than for the ground state. To a certain extent this was to be expected. In molecular orbital approximation the $^3\Sigma_u{}^+$ and $^1\Sigma_u{}^+$ states are represented by $1\sigma_g 1\sigma_u$, and the $^1\Sigma_g{}^+$ state by $1\sigma_g 2\sigma_g$ with some admixture of the $1\sigma_u{}^2$. For such states a wave function with two different α's should do much better than with one α; or in other words, for a single α the expansion lengths we used were probably inadequate. The potential energy curves for these three excited states and the ground state are plotted in Fig. 2.

One point which needs further clarification is the astonishingly good agreement between the calculated and observed dissociation energy for the ground state; such good agreement should occur *after* having made the appropriate corrections for finite nuclear masses. The agreement obtained indicates that this correction is virtually the same for R_e as for infinite separation, where it is known to be 0.0148 ev. Van Vleck[14] calculated this correction for R_e with an approximate wave function and obtained 0.0141 ev. Our good agreement therefore should be considered somewhat fortuitous until this correction has been computed accurately for R_e; this, however, necessitates constructing accurate electronic-vibrational wave functions, which is outside of the scope of this research.

We also computed the potential energy curve for the

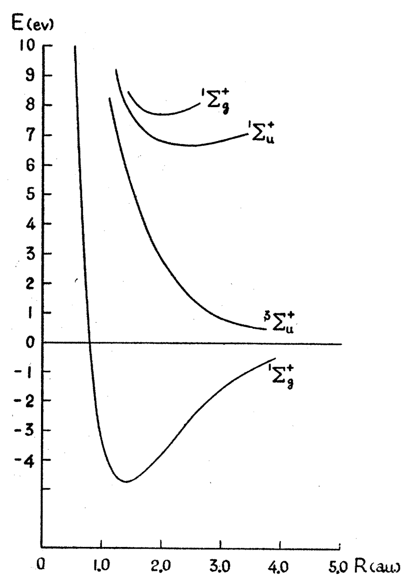

FIG. 2. Computed potential energy curves for H_2.

[14] J. H. Van Vleck, J. Chem. Phys. 4, 327 (1936).

TABLE VIII. Total and potential energies (negative values) for the lowest $^1\Sigma_u{}^+$ state of H_2 computed with 34-term wave functions.

$R\backslash\alpha$	0.55	0.75	0.95	1.15	Interpolated values $-E$(a.u.)	$1+E$(ev)	$V/2E$	α
1.2	0.656343							
	1.698902							
1.4	0.703667	0.694912	0.671639	0.634393	0.703744	8.0611	1.163201	0.5294
	1.641736	1.690720	1.748480	1.812535				
1.6	0.727917	0.726536	0.714628	0.692856	0.728632	7.3839	1.01330	0.6238
	1.589305	1.632007	1.675787	1.727470				
1.8	0.739680	0.742694	0.737242	0.724871	0.742783	6.9988	1.063596	0.7212
	1.551975	1.584736	1.617100	1.657888				
2.0		0.750218	0.748460	0.741828	0.750265	6.7952	1.032531	0.7778
		1.546346	1.570701	1.601620				
2.2		0.752737	0.753182	0.750003	0.753440	6.7088	1.012709	0.8746
		1.513820	1.533895	1.556465				
2.3		0.752769	0.754010	0.751986	0.754033	6.6927	1.005124	0.9260
		1.498859	1.518096	1.537289				
2.4		0.752198	0.754117	0.752984	0.754143	6.6897	0.998332	0.9757
		1.484359	1.503501	1.519947				
2.4429		0.751796	0.753982	0.753166	0.754060	6.6920	0.995534	0.9957
		1.478216	1.497518	1.512985				
2.5		0.751130	0.753658	0.753215	0.753841	6.6979	0.991850	1.0202
		1.470085	1.489753	1.504100				
$R\backslash\alpha$	0.95	1.15	1.35	1.55				
2.6	0.7527437	0.7528455	0.7509885		0.753042	6.7197	0.984883	1.0604
	1.476540	1.489435	1.505081					
2.7	0.7514548	0.7520005	0.7508047		0.752031	6.7472	0.979552	1.1127
	1.463619	1.475656	1.489064					
2.8	0.7498499	0.7507724	0.7500981	0.7478728	0.750777	6.7813	0.974593	1.1656
	1.450795	1.462497	1.474115	1.488773				
3.0		0.7474280	0.7475050	0.7463859	0.747619	6.8672	0.904114	1.2629
		1.437234	1.446544	1.457573				
3.2				0.7433835				
				1.429515				
3.4				0.7393575				
				1.403486				
3.6				0.7346130				
				1.378685				
3.8				0.7293479				
				1.354631				

$He_2{}^{++}$ molecular ion; the results are given in Table XI. The behavior of α a a function of R became somewhat erratic in this case for $R>1.34$; this may be due to the fact that the optimized α for these R values is the result of an extrapolation rather than an interpolation, and calculations for larger values of α seem indicated. Again, time prevented us from investigating this point further.

TABLE IX. Total and potential energies for the first $^1\Sigma_g{}^+$ excited state of H_2, computed with 40-term wave functions.

	$\alpha=0.75$		$\alpha=0.95$	
R(a.u.)	$-E$(a.u.)	$-V$(a.u.)	$-E$(a.u.)	$-V$(a.u.)
1.4	0.681254	1.607352	0.652368	1.667010
1.6	0.705487	1.534631	0.689181	1.576106
1.8	0.714997	1.471155	0.705853	1.502236
1.9	0.716350	1.442075	0.709654	1.470291
2.0	0.716122	1.414470	0.711410	1.441123
2.1	0.714678	1.388229	0.711626	1.414470
2.2	0.712287	1.363310	0.710680	1.390091
2.4	0.705508	1.317670	0.706406	1.347588
2.6	0.697101	1.278861	0.700251	1.313434

The SCF calculations followed very much the same patterns as the calculations with the accurate wave functions just described. Starting with a 5-term SCF function for H_2 for $R=1.4$ obtained previously,[6] we gradually increased this to 9 terms; see Table XII. Note that the cusp value deviates only in the fourth decimal place from its correct value, -1, for the 9-term function. This probably means that our 9-term SCF function, obtained by the expansion method, is equivalent to a solution of the Hartree-Fock integro-dif-

TABLE X. Comparison of calculated and observed equilibrium distances (in A) and energies (relative to two normal H atoms, in ev).

State	$^1\Sigma_g{}^+$	$^1\Sigma_u{}^+$	$^1\Sigma_g{}^+$
E_{calc}	-4.7467	6.6892	7.7153
E_{obs}	-4.7466	6.6220	7.6586
R_{calc}	0.74127	1.258	1.095
R_{obs}	0.74116	1.2926	1.012

TABLE XI. Total and potential energies (negative values) for the ground state of He_2^{++} computed with 40-term wave functions.

$R\diagdown\alpha$	1.55	1.75	1.95	Interpolated values $-E$(a.u.)	$-D$(ev)	$V/2E$	α
0.8		3.356146 8.291381					
1.0	3.599289 7.858302	3.599041 7.860355	3.598095 7.865674	3.599296	10.903	1.091658	1.5789
1.1	3.648290 7.674957	3.648233 7.676450	3.647790 7.679420	3.648314	9.569	1.051899	1.6205
1.2	3.671895 7.515822	3.671960 7.517208	3.671791 7.519510	3.671966	8.926	1.023542	1.7056
1.3	3.679443 7.381839	3.679606 7.383399	3.679628 7.385652	3.679636	8.717	1.003469	1.8814
1.32	3.679608 7.358028	3.679790 7.359673	3.679845 7.361957	3.679845	8.711	1.000285	1.9368
1.34	3.679419 7.335192	3.679621 7.336944	3.679709 7.339272	3.679713	8.715	0.997361	2.0044
1.4	3.677072 7.272398	3.677339 7.274646	3.677521 7.277184	3.677636	8.771	0.990036	2.2785
1.6	3.657536 7.119275	3.658237 7.126460	3.658773 7.131117	3.659397	9.268	0.974326	2.4998
1.8	3.631857 7.031137	3.633829 7.052783	3.635045 7.064212	3.6355	9.92	0.9717	2.1717

ferential equation to an accuracy of four decimal places or better.

Next we computed the SCF function and energy as a function of R, varying and optimizing α for each R; see Table XIII. The α versus R curve for this case practically coincides with the corresponding curve for the accurate ground state function within the limits of accuracy of the optimization of α. The same calculation was carried out for He_2^{++}; the results are collected in Table XIV.

The total *electronic* energy curves for the ground state of H_2, computed with the SCF function and the 40-term expansion, are plotted in Fig. 3; the values at $R=0$

TABLE XII. Convergence of the SCF energy and orbital cusp for H_2 ($\alpha=0.95$, $R=1.4$).

No. of terms	ξ	η	$-E$(a.u.)	D(ev)	Orbital cusp
1	0	0			
2	1	0			
3	2	0			
4	0	2			
5	1	2	1.133571	3.6344	−0.96067
6	3	0	1.133573	3.6345	−0.96192
7	4	0	1.133576	3.6346	−0.96380
8	2	2	1.133604	3.6353	−0.97725
9	0	4	1.133629	3.6360	−0.99989

TABLE XIII. SCF energies (negative values) for the ground state of H_2 computed with 9-term orbitals.

$R\diagdown\alpha$	0.55	0.75	0.95	1.15	1.55	1.95	Interpolated values $-E$(a.u.)	D(ev)	α
0.4	0.078693	0.061186							
0.6	0.729990	0.729544							
0.8	0.980742	0.980734							
1.0	1.085110	1.085138	1.085117				1.085138	2.3166	0.7656
1.2		1.125022	1.125025	1.124987			1.125029	3.4020	0.8629
1.3		1.132015	1.132024	1.132011			1.132024	3.5923	0.9319
1.375		1.133625	1.133641	1.133635			1.133642	3.6364	0.9989
1.400		1.133610	1.133629	1.133625			1.133630	3.6360	1.0162
1.425		1.133355	1.133377	1.133375			1.133379	3.6292	1.0300
1.45		1.132880	1.132906	1.132904			1.132908	3.6164	1.0412
1.5		1.131336	1.131370	1.131371			1.131375	3.5747	1.0560
1.6		1.126285	1.126342	1.126348	1.126239		1.126352	3.4380	1.0701
1.8		1.110810	1.110939	1.110957	1.110927		1.110967	3.0194	1.2826
2.0		1.091319	1.091572	1.091612	1.091611		1.091648	2.4937	1.3476
2.4			1.049143	1.049286	1.049331	1.049282	1.049331	1.3423	1.5432
2.8				1.008214	1.008357	1.008361	1.008376	0.2279	1.7597
3.2				0.971095	0.971443	0.971443	0.971512	−0.7751	1.8265

TABLE XIV. SCF energies (negative values) for the ground state of He_2^{++} computed with 9-term orbitals.

				Interpolated values		
$R\diagdown\alpha$	1.55	1.75	1.95	$-E$(a.u.)	$-D$(ev)	α
0.8	3.309953	3.309683				
1.0	3.545087	3.545052	3.544913	3.545088	12.378	1.583
1.2	3.609087	3.609083	3.609047	3.609089	10.637	1.628
1.3	3.611170	3.611179	3.611160	3.611180	10.580	1.725
1.332	3.609330	3.609344	3.609330	3.609344	10.630	1.750
1.364	3.606548	3.606569	3.606558	3.606569	10.705	1.788
1.6	3.567517	3.567627	3.567665	3.567665	11.764	1.955
1.8	3.523379	3.523675	3.523811	3.523821	12.957	2.020
2.0		3.479477	3.479812			

are known from calculations on He.[15] The ground state *binding* energies for H_2 and He_2^{++}, computed with the SCF function, the 40-term expansion, and the configuration-interaction function determined by McLean et al.,[15a] are plotted in Figs. 4 and 5, respectively. For H_2 above $R=4.0$, our 40-term function becomes inferior to the configuration-interaction function. This is because our wave function is a *polynomial* in ξ and η which requires more and more terms for increasing R in order to approach the correct asymptotic form

$$\exp[-\tfrac{1}{2}R(\xi_1+\xi_2)]\cosh[\tfrac{1}{2}R(\eta_1-\eta_2)].$$

There are two important reasons for obtaining the SCF results. Firstly, the correlation energy, that is, the difference between the SCF energy and the exact energy, is expected to vary smoothly (and often little) when a system undergoes a continuous or small finite physical change. A careful study of the correlation energy in a number of representative cases may open up the possibility of making energy predictions from SCF computations exceeding by far the accuracy of the SCF energies. Secondly, the expectation values of

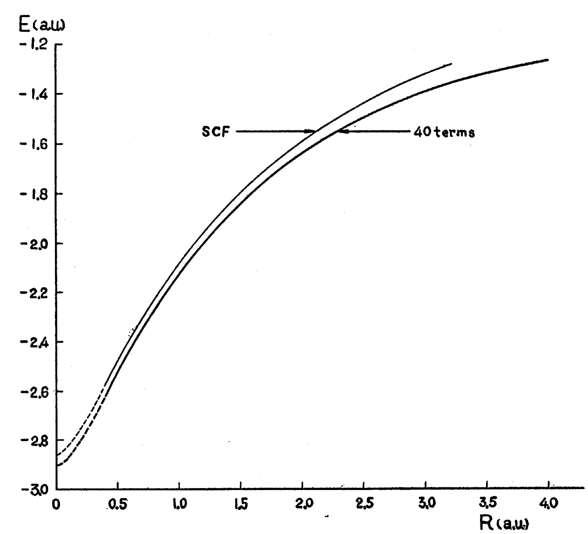

FIG. 3. The electronic energy for the ground state of H_2, computed with the SCF function and the 40-term expansion.

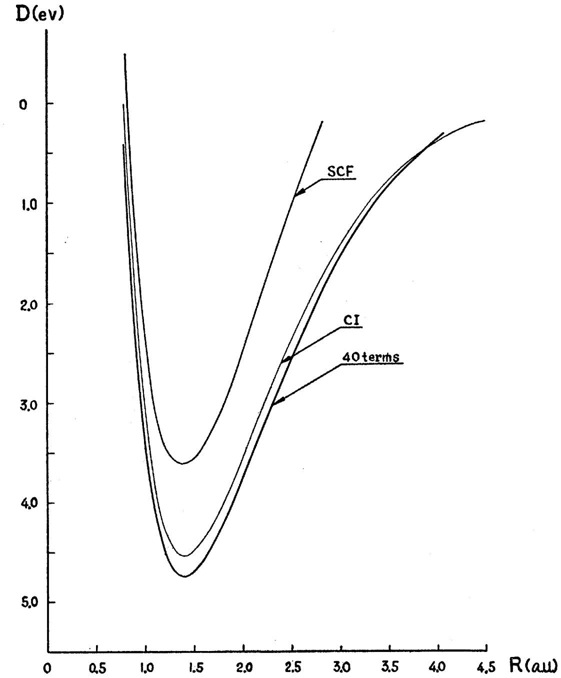

FIG. 4. Potential energy curves for the ground state of H_2 computed with the SCF function, configuration interaction, and the 40-term expansion.

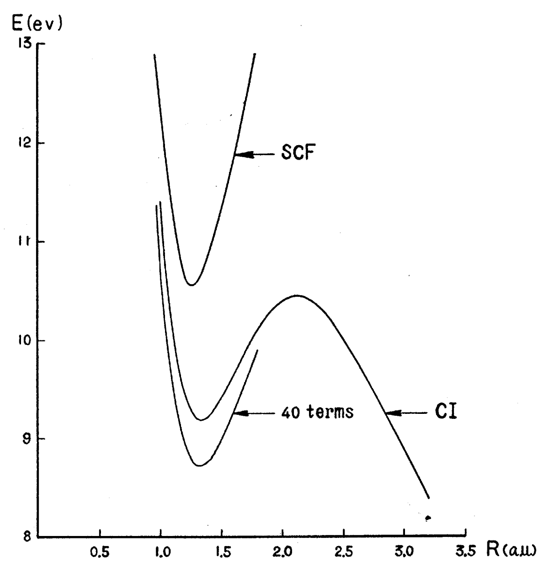

FIG. 5. Potential energy curves for the ground state of He_2^{++} computed with the SCF function, configuration interaction, and the 40-term expansion.

[15] See C. C. J. Roothaan and A. W. Weiss, Revs. Modern Phys. **32**, 194 (1960), this issue; and further footnotes given in that paper. (a) A. D. McLean, A. W. Weiss and M. Yoshimine, Revs. Modern Phys. **32**, 211 (1960), this issue.

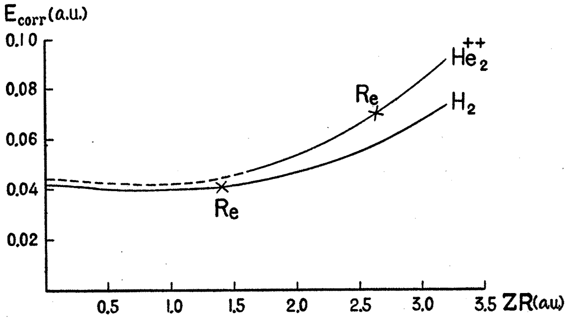

FIG. 6. Correlation energy curves for H_2 and He_2^{++}.

operators which do not explicitly involve the interelectronic distances, in particular, charge distributions and electric moments, may perhaps be rather reliably predicted from the SCF function. In the present case the molecular quadrupole moment and the Larmor terms in the diamagnetic susceptibility are the quantities of interest. In the second and third column of Table XV and in Fig. 6, the correlation energies of H_2 and He_2^{++} are compared. Since the SCF wave function cannot dissociate properly, it becomes a poor wave function for large R, and the correlation energy increases considerably. The correlation energy curves for H_2 and He_2^{++} are very similar only if we plot them against ZR rather than R. In the remaining four columns of Table XV we compare the expectation values $\langle r^2\rangle$ and $\langle 3z^2-r^2\rangle$ for H_2 as computed with our best 28-term function and the 9-term SCF function. Our results for $\langle 3z^2-r^2\rangle$, together with a curve computed by James and Coolidge[5] with a 5-term wave function, are plotted in

TABLE XV. Correlation energies for H_2 and He_2^{++} from 40-term functions and 9-term SCF functions; comparison of $\langle r^2\rangle$ and $\langle 3z^2-r^2\rangle$ for H_2, computed with 28-term functions and 9-term SCF functions.

	Correlarion energy		$\langle r^2\rangle$ for H_2		$\langle 3z^2-r^2\rangle$ for H_2	
ZR	H_2	He_2^{++}	28 terms	9-term SCF	28 terms	9-term SCF
0.00	0.04204	0.04426				
0.60	0.0396					
0.80	0.0393					
1.00	0.03938		2.0488		0.2285	
1.10			2.1710		0.2921	
1.20	0.03990		2.2941	2.3120	0.3629	0.3456
1.30			2.4180	2.4412	0.4370	0.4127
1.35			2.4802		0.4754	
1.40	0.04081		2.5430	2.5736	0.5157	0.4867
1.45			2.6067		0.5587	
1.50			2.6713	2.7095	0.6050	0.5691
1.60	0.04219	0.0465	2.8031	2.8484	0.7081	0.6598
1.70			2.9380		0.8256	
1.80	0.04401		3.0756		0.9577	
2.00	0.04635	0.05388				
2.40	0.05275	0.06288				
2.60		0.06867				
2.80	0.06175					
3.20	0.07331	0.09173				

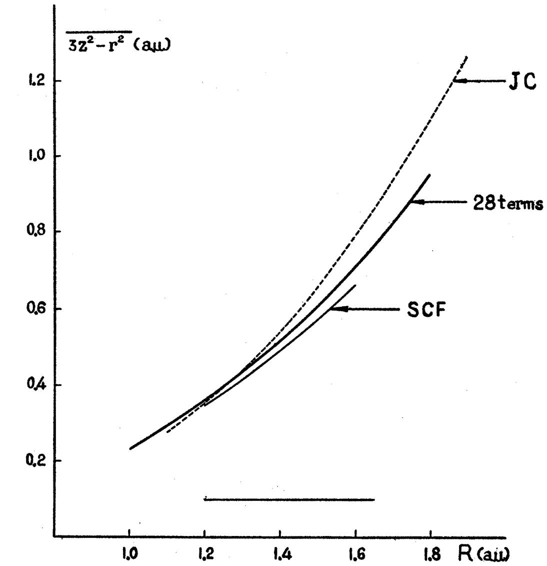

FIG. 7. Expectation values of $\langle 3z^2-r^2\rangle$ computed with the SCF function, a 5-term expansion by James and Coolidge, and our 28-term expansion.

TABLE XVI. Energies and some expectation values for the ground state of H_2, $R=1.4$, computed with various wave functions.

No. of terms	Types of terms: even η	odd η	$\cos(\varphi_1-\varphi_2)$	r_{12}	r_{12}^2	D(ev)	$\langle r^2\rangle$	$\langle 3z^2-r^2\rangle$	$\langle r_{12}^{-1}\rangle$	r_{12}	ξ
21	x					3.8981	2.6160		0.6368	2.0709	2.2338
27	x	x				4.3789	2.5723		0.6077	2.1337	2.2197
40	x	x	x			4.6924					
5	x	x		x		4.6697	2.4609	0.4823	0.5938		2.1917
15	x	x		x		4.7371			0.5876	2.1694	2.2114
24	x	x		x		4.7435			0.5873	2.1703	2.2128
12	x	x		x	x	4.7397	2.5347	0.5227			
20	x	x		x	x	4.7431	2.5408	0.5201			
28	x	x		x	x	4.7443	2.5430	0.5157			
40	x	x		x	x	4.7465			0.5074		2.2127
5-term SCF						3.6344			0.6586	2.0394	2.2222
9-term SCF						3.6360	2.5736	0.4867			

Fig. 7; the horizontal line indicates the classical vibrational "sweep" of the zero-point vibration.

We also explored to some extent the possibilities of superposition of configurations using wave functions defined by Eqs. (1)–(3) with $\mu=0$ and also introduced $\pi_g\pi_g'$ and $\pi_u\pi_u'$ terms as discussed previously. Virtually the same calculation was carried out by Hagstrom[16]; his results are in excellent agreement with ours. In Table XVI we compare some of the more important results of these computations with those obtained with the SCF function and with the wave functions which contain r_{12} explicitly.

[16] S. Hagstrom (unpublished).

ACKNOWLEDGMENTS

We thank Professor H. M. James for his interest in this work and for having provided us with some unpublished details of his early calculations on H_2. Portions of our digital computer program were adapted from codes written by A. D. McLean and A. W. Weiss. We had many stimulating discussions with Dr. R. A. Sack, in the course of which he pointed out several mathematical simplifications.

REVIEWS OF MODERN PHYSICS VOLUME 32, NUMBER 2 APRIL, 1960

Self-Consistent Field Atomic and Molecular Orbitals and Their Approximations as Linear Combinations of Slater-Type Orbitals*

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GLOSSARY OF GENERAL TERMS AND SYMBOLS[1]

Orbital: An adjective used as a noun and introduced as a brief term meaning "one-electron orbital wave function," that is, either an eigenfunction of a one-electron Schrödinger equation or an approximation thereto.[2] It is the nearest quantum mechanical counterpart to the electron orbit of Bohr theory. The practice of referring to "one-electron orbitals," in other words, "one-electron one-electron orbital wave functions" should be discouraged. Could one have a two-electron one-electron orbital wave function?

Spinorbital: This was introduced as a brief term[2] meaning "one-electron wave function including spin." The frequent practice of referring to it as two words "spin orbital" is confusing, suggesting different meanings from that intended. To better indicate the pronunciation, the spelling could perhaps be changed to "spinnorbital."

AO: Central field atomic orbital [cf. Eq. (1)] or, in molecular contexts, sometimes a linear combination (hybrid) of these.

MO: Molecular orbital.

SCF: Self-consistent field.

SCF AO or MO: Cf. Eqs. (1) and (2).

CI: Configuration interaction.

STO: Slater-type orbital [cf. Eq. (3)].

ζ = orbital exponent: The variable parameter in any STO [cf. Eq. (3)].

LC–STO MO: Linear combination of STO's (not necessarily all alike in l but all alike in m or λ) to approximate an MO.

Free-atom MO, free-atom ζ: Terms used in describing LCAO–MO's to indicate that the AO's or the AO ζ values used are the AO's or the ζ's which are suitable (Slater ζ's and AO's) or optimal (best simple AO's) in describing the AO's of free atoms.

LCAO–MO's: MO's approximated by linear combinations of free-atom *or of modified* AO's; since the latter in turn are approximated by LC–STO forms, LCAO MO's in general are most conveniently considered as LC–STO forms.

INTRODUCTION: USES AND LIMITATIONS OF SELF-CONSISTENT FIELD WAVE FUNCTIONS

EVERY exact atomic or molecular wave function must conform to one of the group-theoretical species (taking into account both spin and orbital characteristics) of the appropriate symmetry group. For light atoms and molecules it is sufficient for many purposes to use wave functions in which spin-orbit interaction is neglected, so that each wave function has a definite spin quantum number and a definite orbital species (L, S coupling case for atoms, and the analogous case for molecules).

An exact wave function even of the L, S or L,S-like type does *not* correspond to a single-electron configuration, and exact wave functions are perhaps most convergently represented by linear combinations of

* This work was assisted by a grant from the National Science Foundation.

[1] Tables I and II contain a proposed classification and terminology for various *specific* types of LC–STO approximations to SCF AO's and MO's.

[2] R. S. Mulliken, J. Chem. Phys. **23**, 2005 (1955), Sec. II. 3(b).