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Projected Hartree Product Wavefunctions. III. Comparison with the CI Method for H₂

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from the m . The number of standard tableaux is just $j=1, 2, \dots, j'-1$ columns for the i' th row and then

$$\frac{2S+1}{2k-n+1} \binom{2k-n+1}{k-S-(n/2)},$$

so we must multiply these three numbers together and sum over k from $(n/2)+S$ to n . Thus the total number of independent functions N_F is

$$\begin{aligned} N_F &= \sum_{k=(n/2)+S}^n \frac{2S+1}{2k-n+1} \binom{m}{k} \binom{k}{n-k} \binom{2k-n+1}{k-S-(n/2)} \\ &= \frac{(2S+1)}{(m+1)} \binom{m+1}{(n/2)+S+1} \binom{m+1}{(n/2)-S}. \end{aligned}$$

APPENDIX C: LINEAR INDEPENDENCE OF $\theta NPN_{\sigma_{1k}}$

We here prove the theorem merely stated in Sec. IV of the article that the quantities

$$\theta NPN_{\sigma_{1k}}; \quad k=1, 2, \dots, f(\omega) \quad (C1)$$

are linearly independent in the group algebra. We here again define the σ_{ik} . Let T_1, T_2, \dots, T_f be standard tableaux for which the k th one has the symbol $\alpha(k)_{ij}$ in the i th row and j th column. The tableaux T_k are assumed ordered as follows:

$$\alpha(k)_{ij} = \alpha(k')_{ij}$$

for the rows $i=1, 2, \dots, i'-1$, all columns, and for the

$$\alpha(k)_{i'j'} < \alpha(k')_{i'j'} \quad \text{if } k < k'.$$

Also we let P_i and N_i ; $i=1, \dots, f$ be the positive and negative projectors corresponding to T_i . It is easily seen that if $\alpha(k')_{i'j'} > \alpha(k)_{i'j'}$, then $\alpha(k)_{i''j''} = \alpha(k')_{i'j'}$, where necessarily $i'' > i'$ and $j'' < j'$, i.e., this element appears in a later row and earlier column of T_k . It is also easily seen because of this that (see also Ref. 12)

$$N_i P_j = P_j N_i = 0; \quad j > i. \quad (C2)$$

Equation (C2) is the basis of our proof. Thus we examine

$$\sum_{k=1}^f \gamma_k \theta N_1 P_1 N_1 \sigma_{1k} = 0, \quad (C3)$$

where σ_{1k} is the permutation $\sigma_{1k}^{-1} T_1 \sigma_{1k} = T_k$. Multiplying each term in (C3) on the right by I in the form $\sigma_{1k}(\sigma_{1k})^{-1}$ and on the left by $P_l N_l$ we get

$$\begin{aligned} 0 &= \theta \sum_k \gamma_k \sigma_{1k} N_k P_k N_k P_l N_l, \\ &= \theta' \gamma_l \sigma_{1l} N_l P_l N_l + \theta \sum_{k=l+1}^f \gamma_k \sigma_{1k} N_k P_k N_k P_l N_l, \\ &= \theta' \gamma_f \sigma_{1f} N_f P_f N_f; \quad l=f. \end{aligned} \quad (C4)$$

As we let $l=f, f-1, f-2, \dots, 1$ in turn we see that $\gamma_f, \gamma_{f-1}, \dots, \gamma_1$ are each zero since $\sigma_{1k} N_k P_k N_k \neq 0$. Thus the quantities are linearly independent.

Projected Hartree Product Wavefunctions. III. Comparison with the CI Method for H_2^*

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Calculations of the energy of H_2 have been performed using both the projected Hartree-Fock (PHF) method and a full CI method in the same basis for comparison of the two methods. It is discovered that PHF can account for 86% of the correlation energy, whereas CI will account for 88% of the correlation energy.

I. INTRODUCTION

In two recent articles^{1,2} Gallup has given a spin-free version^{3,4} of the projected Hartree-Fock (PHF)

method originally suggested by Löwdin.⁵ This is an extension of the independent-particle model in which optimization of the orbital functions in a different orbitals for different spins (DODS) trial function is done after the application of all projections necessary to insure the correct symmetry. Thus it has been emphasized by Goddard⁶ and in the first paper of this series, hereinafter denoted as (I)¹ that the use of single-particle orbitals with spatial dissymmetry and what might be called identity dissymmetry can

* This article is based in part on a thesis submitted by R. C. M. to the Graduate Faculty in the University of Nebraska in partial fulfillment of the requirements for the Ph.D. degree.

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¹ G. A. Gallup, J. Chem. Phys. **48**, 1752 (1968).

² G. A. Gallup, J. Chem. Phys. **50**, 1206 (1969), preceding article.

³ F. A. Matsen, Advan. Quant. Chem. **1**, 597 (1964).

⁴ R. D. Poshusta and R. W. Kramling, Phys. Rev. **167**, 139 (1968).

⁵ P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955).

⁶ W. A. Goddard, Phys. Rev. **157**, 73, 81 (1967).

produce a considerable portion of the correlation energy of a multiparticle system.

The adequate testing of the PHF method has had to await the development of larger, high-speed computer systems, and recently a number of computations based on this idea have been done.⁷⁻⁹ As was emphasized in II² the PHF method can be viewed as a form of restricted CI computation and a crucial test of PHF is its comparison to a CI computation using the same fixed basis. In this way the nature and seriousness of the restrictions can be judged.

This article reports such a comparison of the PHF and CI methods for the H₂ molecule.

II. THE PHF CALCULATION

The PHF calculation for H₂ has been done using three different basis sets consisting of STO's, as follows:

$$\text{I: } \{1S_a, 1S_b, 2S_a, 2S_b, 2p\sigma_a, 2p\sigma_b\},$$

$$\text{II: } \{1S_a, 1S_b, 2S_a, 2S_b, 2p\pi_a, 2p\pi_b\},$$

$$\text{III: } \{1S_a, 1S_b, 2S_a, 2S_b, 2p\sigma_a, 2p\sigma_b, 2p\pi_a, 2p\pi_b\},$$

where *a* and *b* refer to the nucleus upon which the orbital is centered. Linear combinations of unnormalized primitive symmetry orbitals are used to form the one-electron wavefunctions. These primitive symmetry orbitals are not all of the same symmetry type and hence the one-electron wavefunctions have spatial dissymmetry.

The one electron functions *U* and *V* are given in general by

$$U = a_1S_{1S} + a_2A_{1S} + a_3S_{2S} + a_4A_{2S} + a_5S_{2p\sigma} + a_6A_{2p\sigma} \\ + a_7S_{2p\pi} + a_8A_{2p\pi},$$

$$V = b_1S_{1S} + b_2A_{1S} + b_3S_{2S} + b_4A_{2S} + b_5S_{2p\sigma} + b_6A_{2p\sigma} \\ + b_7S_{2p\pi} + b_8A_{2p\pi},$$

where

$$S_{1S} = 1S_a + 1S_b,$$

and

$$A_{1S} = 1S_a - 1S_b,$$

etc.

The total molecular wavefunction is obtained by operating on the product of the one-electron functions by a group projection operator,

$$\Psi = e^{(1\Sigma_g^+)} U(1) V(2).$$

The form of the characteristic unit $e^{(1\Sigma_g^+)}$ is given in I.

The coefficients in the orbitals *U* and *V* were

⁷ W. A. Goddard, J. Chem. Phys. **48**, 1008 (1968).

⁸ C. F. Bunge, Phys. Rev. **154**, 70 (1967).

⁹ S. Lunell, Tech. Rept. No. 201, Quantum Chemistry Group, Uppsala, Sweden.

optimized by minimization of the energy expression,

$$E = \frac{\langle e^{(1\Sigma_g^+)} U(1) V(2) | H | e^{(1\Sigma_g^+)} U(1) V(2) \rangle}{\langle e^{(1\Sigma_g^+)} U(1) V(2) | e^{(1\Sigma_g^+)} U(1) V(2) \rangle}, \\ = \frac{\langle U(1) V(2) | H e^{(1\Sigma_g^+)} | U(1) V(2) \rangle}{\langle U(1) V(2) | e^{(1\Sigma_g^+)} | U(1) V(2) \rangle},$$

utilizing an iterative procedure suggested in I. The exponential scale factors in the STO's were also adjusted to optimum values.

The form of the characteristic unit for the Σ_g^+ state of *D_{∞h}* is

$$e^{(\Sigma_g^+)} = (2\pi)^{-1} \int_0^{2\pi} [C_\phi + \sigma_v(\phi) + S_\phi + C_2(\phi)] d\phi.$$

The operators in the integrand are defined as follows:

C_φ is a rotation about the internuclear axis by an angle *φ*,

C₂(φ) is a rotation about a *C₂* axis which intersects the *xz* plane at an angle *φ*,

σ_v(φ) is a reflection through a plane which has an intersection of angle *φ* with the *xz* plane,

S_φ is *σ_hC_φ*, where *σ_h* is a reflection through the plane perpendicular to the internuclear axis.

The functional form of these operators is determined by examining their effect on the atomic orbitals. Since the electron wavefunctions do not contain the *2p_y* functions explicitly, it is necessary to examine the effect of the operators only on the *2p_x* functions. This results in

$$C_\phi 2p_{xa} = \cos\phi 2p_{xa} - \sin\phi 2p_{ya},$$

$$C_2(\phi) 2p_{xa} = \cos 2\phi 2p_{xb} + \sin 2\phi 2p_{ya},$$

$$\sigma_v(\phi) 2p_{xa} = \cos 2\phi 2p_{xa} + \sin 2\phi 2p_{ya},$$

$$S_\phi 2p_{xa} = \cos\phi 2p_{xb} - \sin\phi 2p_{yb}.$$

Placing the functional forms of these operators in the integrand and integrating we obtain

$$e^{(\Sigma_g^+)} S_{2p_x}(1) S_{2p_x}(2) \\ = \frac{1}{2} [S_{2p_x}(1) S_{2p_x}(2) + S_{2p_y}(1) S_{2p_y}(2)],$$

and

$$e^{(\Sigma_g^+)} A_{2p_x}(1) A_{2p_x}(2) \\ = \frac{1}{2} [A_{2p_x}(1) A_{2p_x}(2) + A_{2p_y}(1) A_{2p_y}(2)].$$

These are the $(\pi_u 2p)^2$ and $(\pi_g 2p)^2$ configurations used by McLean, Weiss, and Yoshimine¹⁰ in their configuration-interaction calculation on H₂.

III. THE CI CALCULATION

A full CI calculation has been carried out for each basis set at the equilibrium internuclear distance of

¹⁰ A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. **32**, 211 (1960).

TABLE I. Coefficients and exponential scale factors for the one-electron unprojected wavefunctions at $R=1.4$.

Term	Basis I			Basis II			Basis III		
	<i>U</i>	<i>V</i>		<i>U</i>	<i>V</i>		<i>U</i>	<i>V</i>	
S_{1S}	1.4*	0.7881	0.5674	1.35*	0.6971	0.5218	1.42*	0.7133	0.5353
A_{1S}	1.4	0.5800	-0.4645	1.35	0.5745	-0.4332	1.42	0.5340	-0.4170
S_{2S}	1.2	-0.07330	0.6619	1.23	-0.1192	0.6669	1.22	-0.04799	0.6502
A_{2S}	1.2	0.1519	-0.1216	1.23	0.1412	-0.1065	1.22	0.1294	-0.1005
$S_{2p\sigma}$	2.1	0.1139	-0.09298	0.0	0.0	0.0	2.05	0.1096	-0.09079
$A_{2p\sigma}$	2.1	-0.03223	0.02583	0.0	0.0	0.0	2.05	-0.03413	0.02691
$S_{2p\pi}$	0.0	0.0	0.0	1.73	0.2901	-0.2171	1.72	0.3127	-0.2347
$A_{2p\pi}$	0.0	0.0	0.0	1.73	0.2563	-0.1918	1.72	-0.2756	0.2068

*These columns give the STO exponent scale factors.

$R=1.4$ a.u. The 14-term CI wavefunction for basis set III may be written as

$$\Psi_{III} = C_1(S_{1S}S_{1S}) + C_2(S_{1S}S_{1S}) + C_3(A_{1S}A_{1S}) + C_4(S_{2p\sigma}S_{2p\sigma}) + C_5(A_{2p\pi}A_{2p\pi}) + C_6(S_{2S}S_{2p\sigma}) + C_7(A_{1S}A_{2S}) + C_8(A_{2S}A_{2S}) + C_9(S_{2S}S_{2S}) + C_{10}(A_{2S}A_{2p\sigma}) + C_{11}(A_{1S}A_{2p\sigma}) + C_{12}(S_{1S}S_{2p\sigma}) + C_{13}(A_{2p\sigma}A_{2p\sigma}) + C_{14}(S_{2p\sigma}S_{2p\sigma}),$$

where

$$(\psi_1, \psi_2) = \frac{1}{2}[\psi_1(1)\psi_2(2) + \psi_2(1)\psi_1(2)]$$

and

$$(\psi_{p\pi}\psi_{p\pi}) = \frac{1}{2}[\psi_{p\pi}(1)\psi_{p\pi}(2) + \psi_{p\pi}(1)\psi_{p\pi}(2)].$$

The exponential scale factors were not optimized for the CI wavefunctions, but those scale factors which were optimal for the PHF wavefunction were used in the corresponding CI wavefunction. For Ψ_{III} the coefficients are arranged in decreasing order so that C_1 has the greatest magnitude and C_{14} the smallest. Ψ_I and Ψ_{II} are formed by setting the appropriate $C_i=0$.

IV. RESULTS AND DISCUSSION

The coefficients in each of the orbitals U and V are given in Table I, and the coefficients of the configurational terms as calculated by the PHF methods and the CI method are listed in Table II for each basis set. The table is arranged so that the co-

TABLE II. Coefficients obtained by PHF and CI methods.

PHF Coeff.	CI Coeff.	Config.	Set I		Set II		Set III	
			PHF	CI	PHF	CI	PHF	CI
$(a_1b_3 + a_3b_1)/2$	C_1	$(S_{1S}S_{2S})$	0.4117	0.6661	0.4054	0.6392	0.4369	0.6971
a_1b_1	C_2	$(S_{1S}S_{1S})$	0.7670	0.5585	0.7324	0.5816	0.7616	0.5453
a_2b_2	C_3	$(A_{1S}A_{1S})$	-0.4622	-0.4230	-0.5011	-0.4195	-0.4442	-0.4080
$a_7b_7/2$	C_4	$(S_{2p\pi}S_{2p\pi})$	0.0	0.0	-0.6341	-0.09983	-0.07319	-0.1093
$a_8b_8/2$	C_5	$(A_{2p\pi}A_{2p\pi})$	0.0	0.0	-0.04948	-0.07368	-0.05683	-0.08298
$(a_3b_5 + a_5b_3)/2$	C_6	$S_{2S}S_{2p\sigma}$	0.07049	0.07244	0.0	0.0	0.07542	0.07836
$a_2b_4 + a_4b_2)/2$	C_7	$(A_{1S}A_{2S})$	-0.1210	-0.06569	-0.1232	-0.07086	-0.1073	-0.07817
a_5b_4	C_8	$(A_{2S}A_{2S})$	-0.03167	-0.04704	-0.03029	-0.2025	-0.02594	-0.07410
a_8b_3	C_9	$(S_{2S}S_{2S})$	-0.08322	0.03251	-0.1600	-0.1254	-0.06224	-0.06278
$(a_4b_6 + a_6b_4)/2$	C_{10}	$(A_{2S}A_{2p\sigma})$	0.006725	0.01597	0.0	0.0	0.006893	0.05666
$(a_2b_6 + a_6b_2)/2$	C_{11}	$(A_{1S}A_{2p\sigma})$	0.02569	-0.2104	0.0	0.0	0.02853	-0.05652
$(a_1b_5 + a_5b_1)/2$	C_{12}	$(S_{1S}S_{2p\sigma})$	-0.007434	-0.07892	0.0	0.0	-0.006075	0.03540
a_6b_5	C_{13}	$(A_{2p\sigma}A_{2p\sigma})$	-0.001428	-0.03184	0.0	0.0	-0.001832	-0.03167
a_8b_6	C_{14}	$(S_{2p\sigma}S_{2p\sigma})$	-0.1816	-0.03023	0.0	0.0	-0.01985	-0.03137

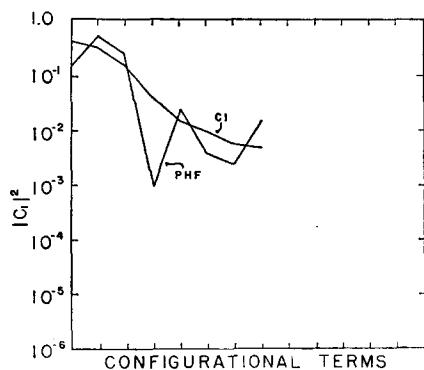


FIG. 1. Graph of $|C_i|^2$ for PHF and CI methods for basis set I. The CI coefficients determine the configuration ordering.

efficients of the 14-term CI wavefunction for basis set III are listed in decreasing order of absolute magnitude. In Column 1 the relationships between the coefficients of the one-electron unprojected wavefunctions U and V and the coefficients of the CI wavefunction in Column 2 are given.

For ease of comparing the linear coefficients C_i calculated by the CI methods and those calculated by the PHF method, graphs of the squares of the coefficients were made. Figures 1-3 are for basis sets I, II, and III, respectively. It might be expected that in a good approximation to the full CI wavefunction for a given basis set, the squares of the coefficients might be about the same relative size, or at least have about the same type of ordering of the configurations with respect to the absolute magnitude of the coefficients. From Figs. 1-3, however, it is seen that the order of the squares of the coefficients is rather drastically changed for the two methods. The logarithmic scale overemphasizes the differences among the smaller coefficients, of course.

For basis set II one might expect the PHF and the CI methods to give equivalent results since there is not a restriction on the number of linear coefficients to be varied when going from the CI to the PHF method. Figure 2 shows, however, that the two

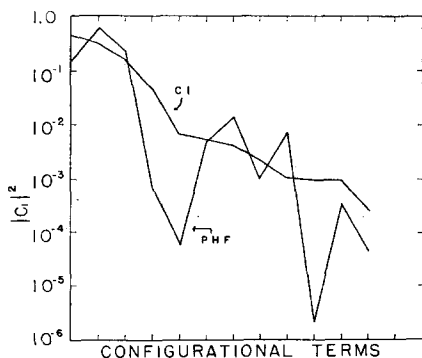


FIG. 2. Graph of $|C_i|^2$ for PHF and CI methods for basis set II. The CI coefficients determine the configuration ordering.

TABLE III. Energies and $\% E_{\text{corr}}$ for different basis sets and PHF and CI methods at $R=1.40$ a.u.

Method	Basis	Total energy (a.u.)	$\% E_{\text{corr}}$
PHF	I	-1.15828	60
CI	I	-1.15929	63
PHF	II	-1.16253	71
CI	II	-1.16274	71
PHF	III	-1.16875	86
CI	III	-1.16955	88

methods are not equivalent, and closer examination reveals that the one electron unprojected wavefunctions must contain complex coefficients in order for the PHF wavefunction to be equivalent to the CI wavefunction in this particular case.

The restriction of requiring the coefficients in the one-electron functions to be real causes in some cases a change in the order of the size of the coefficients obtained with the PHF method from those obtained with the CI method. The reality constraint can also cause some configurations which are relatively unimportant in the CI wavefunction to become more important in the PHF method, but apparently does not result in a serious raising of the total energy as can be seen from Table III.

The larger energy differences between the PHF and CI methods for basis sets I and III are apparently due to the fact that there are more linear coefficients which can be varied in the CI wavefunctions than in the PHF wavefunctions.

The PHF energy basis I from Table III can be compared with the energy of -1.151526 a.u. obtained by Goddard⁶ with his $G1$ method. A restriction imposed by Goddard requires the one-electron functions to be reflections of one another. This restriction has been removed in the present calculation and ap-

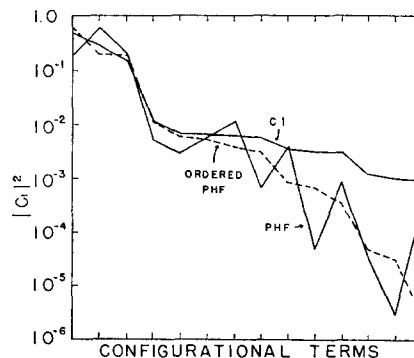


FIG. 3. Graph of $|C_i|^2$ for PHF and CI methods for basis set III. The CI coefficients determine the configuration ordering for the solid lines. The dashed line is the PHF coefficients ordered.

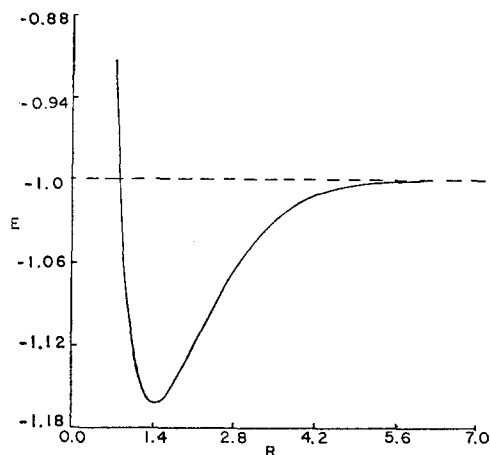


FIG. 4. Graph of interatomic potential curve for basis II. Both coordinates are in atomic units.

parently accounts for a lowering in the energy of almost 0.007 a.u.

It is also apparent from Table III that the PHF wavefunction is able to account for a large part of the correlation energy, 86% for the PHF method basis set III as compared to 88% for the CI wavefunction. By comparing the energy values obtained using set I with those obtained using basis II we see that the effect of adding $2p_x$ functions to a basis set containing $1S$ and $2S$ functions is greater than the effect of adding $2p_z$ functions. This indicates that the addition of functions which account for angular correlation is more important than the addition of more functions which account for left-right correlation.

Although there is some restriction among the coefficients for the PHF wavefunction, it is still a close approximation to the CI wavefunction. Of course the PHF method has the advantage for larger systems of using all configurations where it might not be practical to include all the possible configurations in a full CI calculation. In such cases the configurations used for a truncated CI calculation may require the application of intuition for their selection, whereas the PHF method is capable of including all configurations, giving more weight to the most important ones via the variation principle.

The interatomic potential curve is illustrated in Fig. 4 for basis II. It shows that the PHF method is able to account for proper dissociation of the hydrogen molecule into two hydrogen atoms. The complete potential curve was not calculated for basis III.

A further test of the quality of the PHF wave-

function with basis set II can be obtained by computing the molecular vibrational frequency. This was done by fitting an eight-degree polynomial to the internuclear potential curve near the minimum with a resulting frequency of 4460 cm^{-1} .¹¹ This is in satisfactory agreement with the experimental value of 4401 cm^{-1} ,¹² although not as good as the best calculated value 4401.4 cm^{-1} obtained by Baran and Kolos.¹³

V. SUMMARY AND CONCLUSIONS

Linear combinations of primitive symmetry orbitals of different symmetry types can be used to form one-particle wavefunctions. These one-particle functions have spatial dissymmetry as compared to functions made up of symmetry orbitals of one symmetry type. A characteristic unit of the Kronecker product of the spatial symmetry operations and the group of exchange symmetry operations is used as a projection operator to project out the desired symmetry components from a product of the one-electron functions. The results obtainable from the PHF method are comparable to those obtained by carrying out a full CI calculation. The PHF method should be capable of reducing the work necessary to obtain accurate wavefunctions for many electron systems. This reduction of work is a result in the PHF method of the capability of varying independent-particle orbitals separately in an iterative process rather than varying all the coefficients of the configurations in a full CI calculation. The PHF method should make it possible to compute properties of atoms and molecules to a higher degree of accuracy than has been hertofore attainable by approximate methods.

The relative computation times for the two methods appear about the same, depending on the trial vectors used in the PHF method. The manipulations of the matrices in the PHF method are certainly more involved than in the CI method. This is somewhat offset by the fact that the CI method involves larger matrices.

ACKNOWLEDGMENT

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¹¹ J. L. Dunham, *Phys. Rev.* **41**, 721 (1932).

¹² B. P. Stoicheff, *Can. J. Phys.* **35**, 730 (1957).

¹³ J. Baran and W. Kolos, *J. Mol. Spectry* **8**, 121 (1962).