

Electron-Coupled Interaction between Nuclear Spins in HD Molecule*

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(Received March 7, 1958)

Electron-coupled interaction between two nuclear spins \mathbf{I}_A and \mathbf{I}_B is of the form $\hbar\delta_{AB}\mathbf{I}_A\cdot\mathbf{I}_B$. In this paper, formulas for calculating δ_{AB} are derived by using the variational method. By using these formulas, we have calculated δ_{AB} of the HD molecule at internuclear distances of 1.3, 1.4, and 1.5 atomic units. The total wave function was chosen as a linear combination of seven independent functions of ${}^2\Sigma_g^+$ symmetry, representing the unperturbed state, and several additional functions, to represent the perturbation. The average value of δ_{AB} over the zero-point vibration, $\langle\delta_{AB}\rangle_{00}$, is found to be 37.138 cps. Further, the refinement of a part of the calculations is undertaken by use of the 11-term James and Coolidge wave function. The final result is $\langle\delta_{AB}\rangle_{00}=35.217$ cps. The agreement with the observed value of 42.7 ± 0.7 cps is satisfactory, considering that we have used only a few terms for the additional perturbative wave function and that the result is a sum of terms which cancel each other appreciably. Contributions from each perturbing Hamiltonian and also from a set of wave functions with different symmetry character were obtained separately. The various results are presented and discussed.

INTRODUCTION

RAMSEY¹ has shown that the interaction in a molecule between two nuclear spins, \mathbf{I}_A and \mathbf{I}_B , of the form

$$\hbar\delta_{AB}\mathbf{I}_A\cdot\mathbf{I}_B,$$

can be derived via the magnetic interaction between the nuclei and the electrons. He estimated the value of the constant δ_{AB} for the HD molecule and obtained a reasonable result. However, as his estimation was based on second-order perturbation theory, he was obliged to use some drastic approximations to the summation over the excited states.

On the other hand, by use of the variational method we have succeeded in overcoming similar difficulties² involved in calculating the electric polarizabilities,³ the magnetic susceptibilities, etc.,⁴ of the hydrogen molecule. In this paper, we will show that this method can also be applied for the calculation of δ_{AB} for the HD molecule. It must be noted especially that not only the contributions from each term of the perturbing Hamiltonian but also the contributions due to the mixing of the set of wave functions of each symmetry type can be obtained separately.

Recently, Stephen⁵ calculated δ_{AB} of the HD molecule by using the variational method. The main differences between his calculations and ours are the following:

(a) He used a wave function of the form $\Phi_0(1+\Phi_1')$, whereas we have employed the more flexible form

$\Phi_0+\Phi_1$, where Φ_0 is the unperturbed function. Hence his formulation is somewhat different from ours.

(b) As Φ_0 , he used a very simple V.B. or M.O. wave function, compared with our more exact solution.

(c) He did not discuss the separate contributions due to the mixing of the wave functions of different symmetry type.

(d) He did not treat the nuclear magnetic moments as quantum-mechanical vector operators.

FORMULAS FOR CALCULATING δ_{AB}

Adopting the notation given in Ramsey's paper,¹ the Hamiltonian of the HD molecule in the adiabatic approximation can be expressed as follows:

$$H = H^0 + \gamma_A H^A + \gamma_B H^B + \gamma_A^2 H^{AA} + \gamma_B^2 H^{BB} + \gamma_A \gamma_B H^{AB}. \quad (1)$$

Here A and B denote the proton and the deuteron in the HD molecule, respectively; H^0 is the Hamiltonian describing the motion of the two electrons in the Coulomb field of the two nuclei, and

$$H^A = H_1^A + H_2^A + H_3^A, \quad (2)$$

where

$$H_1^A = (e\hbar^2/mci) \sum_j \{ \mathbf{r}_{jA}^{-3} \mathbf{I}_A \times \mathbf{r}_{jA} \cdot \nabla_j \}, \quad (2.1)$$

$$H_2^A = 2\beta\hbar \sum_j \{ 3\mathbf{r}_{jA}^{-5} (\mathbf{S}_j \cdot \mathbf{r}_{jA}) (\mathbf{I}_A \cdot \mathbf{r}_{jA}) - \mathbf{r}_{jA}^{-3} \mathbf{S}_j \cdot \mathbf{I}_A \}, \quad (2.2)$$

$$H_3^A = (16\pi\beta\hbar/3) \sum_j \delta(\mathbf{r}_{jA}) \mathbf{S}_j \cdot \mathbf{I}_A. \quad (2.3)$$

Further H^{AB} is given by

$$H^{AB} = H_1^{AB} + H_4^{AB}, \quad (3)$$

where

$$H_1^{AB} = (e^2\hbar^2/mc^2) \sum_j \mathbf{r}_{jA}^{-3} \mathbf{r}_{jB}^{-3} \times (\mathbf{I}_A \times \mathbf{r}_{jA}) (\mathbf{I}_B \times \mathbf{r}_{jB}), \quad (3.1)$$

* Supported in part by the Office of Naval Research under contract with the Massachusetts Institute of Technology.

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¹ N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

² W. Weltner, J. Chem. Phys. **28**, 477 (1958).

³ Ishiguro, Arai, Mizushima, and Kotani, Proc. Phys. Soc. (London) **A65**, 178 (1952).

⁴ E. Ishiguro and S. Koide, Phys. Rev. **94**, 350 (1954).

⁵ M. J. Stephen, Proc. Roy. Soc. (London) **A243**, 264 and 174 (1957).

$$H_A^{AB} = -\hbar^2 \{ 3R_{AB}^{-5} (\mathbf{I}_A \cdot \mathbf{R}_{AB}) (\mathbf{I}_B \times \mathbf{R}_{AB}) - R_{AB}^{-3} \mathbf{I}_A \cdot \mathbf{I}_B \}, \quad (3.2)$$

and

$$H^{AA} = (e^2 \hbar^2 / 2mc^2) \sum_j \{ \mathbf{r}_{jA}^{-3} \mathbf{I}_A \times \mathbf{r}_{jA} \}^2. \quad (4)$$

H^B and H^{BB} can be given by (2) and (4), respectively, *mutatis mutandis*.

Now we intend to solve the eigenvalue problem for the Hamiltonian (1) by the Ritz variational method, considering those terms involving γ_A and γ_B small compared to H^0 . The formulation can be performed quite analogously to those previously given.^{3,4}

Since, however, the perturbing Hamiltonian (2) depends on the electron spin as well as on the electronic spatial coordinates, the wave functions corresponding to the triplet states, which differ in spin from the $^1\Sigma_g^+$ ground state and hence did not have to be taken into account in the previous cases,^{3,4} must now also be taken into account along with the singlet states. It must be mentioned, moreover, that \mathbf{I}_A and \mathbf{I}_B are the quantum-mechanical vector operators rather than the ordinary c numbers, and so in order to apply the variational principle to the present problem unambiguously, it is best to introduce a certain representation for these operators. With these remarks in mind, we have treated the problem in the following way:

In the first place, the eigenfunction for H^0 is supposed to be

$$\Phi_0 = \sum_i c_i \theta_i \Theta_0, \quad (5)$$

where the θ_i ($i=1, 2, \dots$) are the linearly independent functions of the space coordinates of the two electrons with Σ_g^+ symmetry and Θ_0 is the spin eigenfunction corresponding to the singlet. Secondly, we assume that on account of certain terms, such as the terms representing the interaction between the external magnetic field and the nuclear spins, the system of the two nuclei is quantized and has the eigenfunction χ_l ($l=0, 1, 2, \dots$). Then our eigenfunction may be written as follows:

$$\Psi = \sum_i c_i \theta_i \Theta_0 \chi_0 + \gamma_A \sum_{k,l} a_{k,l} \varphi_k \Theta_k \chi_l + \gamma_B \sum_{k,l} b_{k,l} \varphi_k \Theta_k \chi_l. \quad (6)$$

Here, the φ_k and Θ_k are functions of the space and spin coordinates of the two electrons, respectively. It is sufficient to consider as $\varphi_k \Theta_k$ only those functions which have different symmetry character (with respect to the symmetry operations of the molecule) from those of $\theta_i \Theta_0$, that is, $^1\Sigma_g^+$ symmetry. c_i , $a_{k,l}$, and $b_{k,l}$ are the coefficients to be determined by the variational principle. For simplicity, the set of letters k and l is abbreviated as K in the following.

Following similar procedures to those developed in references 3 and 4, we can derive the relation

$$c_i = c_i^0 + \gamma_A^2 c_i^1 + \gamma_B^2 c_i^2 + \gamma_A \gamma_B c_i^3 + \dots, \quad (7)$$

and the equations determining the coefficients a_K and b_K :

$$\sum_{K'} (H_{KK'}^0 - E_0 S_{KK'}) a_{K'} = - \sum_i H_{K_i^A} c_i^0, \quad (8.1)$$

$$\sum_{K'} (H_{KK'}^0 - E_0 S_{KK'}) b_{K'} = - \sum_i H_{K_i^B} c_i^0, \quad (8.2)$$

where

$$E_0 = \sum_{i,i'} c_i^0 c_{i'}^0 H_{i,i'}, \quad (9)$$

and $H_{K_i^A}$, $H_{K_i^B}$, $H_{KK'}^0$, $H_{i,i'}$, and $S_{KK'}$ are the matrix elements of H^A , H^B , H^0 , and unity with respect to the appropriate functions $K(\varphi_k \Theta_k \chi_l)$, $K'(\varphi_{k'} \Theta_{k'} \chi_{l'})$, $i(\theta_i \Theta_0 \chi_0)$, and $i'(\theta_{i'} \Theta_0 \chi_0)$.

Now we introduce the coordinate axes ξ , η , and ζ fixed in the framework of the molecule. The origin of these axes is the midpoint of the two nuclei. The ζ axis is taken to be parallel to the direction from A to B . Then we can write

$$H^N = \sum_{\xi} I_{N\xi} H^{N\xi}, \quad (N=A \text{ or } B), \quad (10)$$

where $I_{N\xi}$ is the ξ component of the spin of the nucleus N , $H^{N\xi}$ does not contain the nuclear spin operators, and \sum_{ξ} means the sum over ξ , η , and ζ . Further, by putting

$$a_K = \sum_{\xi} \langle \chi_l | I_{A\xi} | \chi_0 \rangle a_{K\xi}, \quad (11.1)$$

$$b_K = \sum_{\xi} \langle \chi_l | I_{B\xi} | \chi_0 \rangle b_{K\xi}, \quad (11.2)$$

we can reduce Eqs. (8.1) and (8.2) as follows:

$$\sum_{k'} (H_{kk'}^0 - E_0 S_{kk'}) a_{k'\xi} = - \sum_i H_{k_i^A} c_i^0, \quad (12.1)$$

$$\sum_{k'} (H_{kk'}^0 - E_0 S_{kk'}) b_{k'\xi} = - \sum_i H_{k_i^B} c_i^0, \quad (12.2)$$

where ξ here is used to represent ξ , η , or ζ . Since the nuclear spins are eliminated entirely from Eq. (12), we can write $H_{k_i^A}$, $a_{k\xi}$, \dots , instead of $H_{K_i^A}$, $a_{K\xi}$, \dots , respectively. We have made use of this fact in advance in Eq. (11).

The expectation value of the Hamiltonian (1) with respect to the wave function (6) becomes

$$\begin{aligned} E = E_0 & + \gamma_A^2 [\sum_{i,i'} c_i^0 c_{i'}^0 H_{i,i'}^{AA} + \sum_{\xi,\eta} \langle \chi_0 | I_{A\xi} I_{A\eta} | \chi_0 \rangle \bar{\delta}_{AA}^{\xi\eta}] \\ & + \gamma_B^2 [\sum_{i,i'} c_i^0 c_{i'}^0 H_{i,i'}^{BB} + \sum_{\xi,\eta} \langle \chi_0 | I_{B\xi} I_{B\eta} | \chi_0 \rangle \bar{\delta}_{BB}^{\xi\eta}] \\ & + \gamma_A \gamma_B [\sum_{i,i'} c_i^0 c_{i'}^0 H_{i,i'}^{AB} \\ & + \sum_{\xi,\eta} \langle \chi_0 | I_{A\xi} I_{B\eta} | \chi_0 \rangle \bar{\delta}_{AB}^{\xi\eta}] + \dots, \quad (13) \end{aligned}$$

where, for example,

$$\bar{\delta}_{AA}^{\xi\eta} = \sum_{i,k} c_i^0 H_{i,k}^{A\xi} a_{k\eta}, \quad (14.1)$$

$$\bar{\delta}_{AB}^{\xi\eta} = \sum_{i,k} c_i^0 H_{i,k}^{A\xi} b_{k\eta} + \sum_{i,k} c_i^0 H_{i,k}^{B\eta} a_{k\xi}. \quad (14.2)$$

Since H^{AB} can be expressed as $H^{AB} = \sum_{\xi,\eta} I_{A\xi} I_{B\eta} H^{AB\xi\eta}$, we can write the fourth term of (13) as $\langle \chi_0 | E_{AB} | \chi_0 \rangle$, where

$$E_{AB} = \hbar \mathbf{I}_A \cdot \bar{\delta}_{AB} \cdot \mathbf{I}_B + \hbar \bar{\delta}_{AB} \mathbf{I}_A \cdot \mathbf{I}_B. \quad (15)$$

TABLE I. Orbital part of the additional wave function φ_k .^{a-c}

Symmetry	$\varphi_k / \left\{ \frac{1}{2\pi} \exp[-\delta(\lambda_1 + \lambda_2)] \right\}$, ($\delta = 0.75$)
$^1\Sigma_g^-$	$(\lambda_1 - \lambda_2)[(\lambda_1^2 - 1)(1 - \mu_1^2)(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}} \sin(\varphi_1 - \varphi_2)$
$^1\Sigma_u^-$	$(\mu_1 - \mu_2)[(\lambda_1^2 - 1)(1 - \mu_1^2)(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}} \sin(\varphi_1 - \varphi_2)$
$^3\Sigma_g^+$	$(\lambda_1 - \lambda_2); (\mu_1^2 - \mu_2^2)$
$^3\Sigma_u^+$	$(\mu_1 - \mu_2); (\lambda_1\mu_1 - \lambda_2\mu_2); (\lambda_1\mu_2 - \lambda_2\mu_1)$
$^1,^3\Pi_g$	$\mu_1[(\lambda_1^2 - 1)(1 - \mu_1^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_1}{\cos \varphi_1} \right\} \pm \mu_2[(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_2}{\cos \varphi_2} \right\};$ $\mu_2[(\lambda_1^2 - 1)(1 - \mu_1^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_1}{\cos \varphi_1} \right\} \pm \mu_1[(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_2}{\cos \varphi_2} \right\}$
$^1,^3\Pi_u$	$[(\lambda_1^2 - 1)(1 - \mu_1^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_1}{\cos \varphi_1} \right\} \pm [(\lambda_2^2 - 1)(1 - \mu_2^2)]^{\frac{1}{2}} \left\{ \frac{\sin \varphi_2}{\cos \varphi_2} \right\}$
$^3\Delta_g$	$(\lambda_1^2 - 1)(1 - \mu_1^2) \left\{ \frac{\sin 2\varphi_1}{\cos 2\varphi_1} \right\} - (\lambda_2^2 - 1)(1 - \mu_2^2) \left\{ \frac{\sin 2\varphi_2}{\cos 2\varphi_2} \right\}$
$^3\Delta_u$	$\mu_1(\lambda_1^2 - 1)(1 - \mu_1^2) \left\{ \frac{\sin 2\varphi_1}{\cos 2\varphi_1} \right\} - \mu_2(\lambda_2^2 - 1)(1 - \mu_2^2) \left\{ \frac{\sin 2\varphi_2}{\cos 2\varphi_2} \right\};$ $\mu_2(\lambda_1^2 - 1)(1 - \mu_1^2) \left\{ \frac{\sin 2\varphi_1}{\cos 2\varphi_1} \right\} - \mu_1(\lambda_2^2 - 1)(1 - \mu_2^2) \left\{ \frac{\sin 2\varphi_2}{\cos 2\varphi_2} \right\}$

^a λ , μ , and φ are elliptic coordinates.

^b Where \pm signs occur, + corresponds to singlet, - to triplet.

^c The formulas containing the curly brackets should be understood as representing the two kinds of functions, namely, the one with the sine and the other with the cosine throughout.

In this way we can derive the same formulas as given by Ramsey.¹ The expressions for δ_{AB} can be found easily as follows:

$$\delta_{AB} = (\gamma_A \gamma_B / 3h) \sum_{\xi} \{ \sum_{i, i'} c_i^0 c_{i'}^0 H_{i, i'}^{AB \xi \xi} + \bar{\delta}_{AB} \xi \xi \}. \quad (16)$$

Since the contribution of H_4^{AB} to δ_{AB} vanishes, we must take into account only H_1^{AB} in the first term of (16).

CALCULATIONS AND RESULTS

As the unperturbed wave function Φ_0 , we have adopted the 7-term function obtained by the present author^{4,6,7} for the values of the internuclear distance of 1.3, 1.4, and 1.5 atomic units (au). As to the additional wave functions $\varphi_k \Theta_k$, we can see from the symmetry properties of the perturbing Hamiltonian that we must take into account only the functions with the symmetry character of $^1\Sigma_g^-$, $^1\Sigma_u^-$, $^1\Pi_g$, $^1\Pi_u$, $^3\Sigma_g^+$, $^3\Sigma_u^-$, $^3\Pi_g$, $^3\Pi_u$, $^3\Delta_g$, and $^3\Delta_u$. More precisely, the singlet functions among them are connected by the presence of the perturbing Hamiltonian H_1^A and H_1^B , and the triplet functions are connected by the presence of H_2^A and H_2^B . $^3\Sigma_g^+$ and $^3\Sigma_u^-$ arise also from H_3^A and H_3^B .

Since it is our aim to survey the usefulness of the variational method in the calculation of δ_{AB} and to discuss the features of the different kinds of contributions to it by making a preliminary calculation rather than to calculate the most accurate value of δ_{AB} , we

are content to employ only a small number of functions for each symmetry state. The functions adopted are given in Table I, and were chosen mainly because of the computational requirements of simplicity and convenience.

The matrix elements H_{ki}^A , H_{ki}^B , \dots can be calculated quite analogously to the way described in the previous papers.^{3,4,6,7} Then $a_{k\xi}$, $b_{k\xi}$, \dots can be obtained by solving Eq. (12). By inserting these values in Eqs. (14.2) and (16), we can find the numerical values of δ_{AB} . Contributions to δ_{AB} , due to the set of additional functions of each symmetry character in the presence of a different perturbing Hamiltonian, can be calculated separately and are denoted as $\delta_{1AB}(^3\Sigma_g^+)$, $\delta_{2AB}(^3\Sigma_g^+)$, \dots . The results are given in Table II.

From Table II, we can see that, as pointed out by Ramsey,¹ the value of δ_{AB} can be found mainly from δ_{3AB} , the contributions due to H_3^A and H_3^B . Fortunately, moreover, δ_{3AB} can be calculated much more easily than the other contributions. For these reasons, we have undertaken to improve the calculation of δ_{3AB} by adopting, as an unperturbed wave function Φ_0 , the familiar 11-term James and Coolidge function ($\delta = 0.75$).⁸ As the additional perturbative wave functions, we have, however, again used the same ones as above. The results are given in Table III.

Finally, we have calculated $\langle \delta_{AB} \rangle_{00}$, the average value

⁶ E. Ishiguro, J. Phys. Soc. Japan 3, 129 (1948).

⁷ E. Ishiguro, J. Phys. Soc. Japan 3, 133 (1948).

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

TABLE II. Contribution to δ_{AB} (in units of cps) from each set of additional wave functions with different symmetry and from the different terms of the perturbing Hamiltonian.^a

Perturbing Hamiltonian	Symmetry of additional function	Notation for each contribution	δ_{AB} $R_{AB}(\text{au})$				δ_{AB}		
			1.3	1.4	1.5	$\langle\delta_{AB}\rangle_{00}^b$	Stephen ^c V.B.	M.O.	Ramsey ^d
$H_3^A+H_3^B$	${}^3\Sigma_g^+$	$\delta_{3AB}({}^3\Sigma_g^+)$	-79.065	-64.433	-52.611	-63.165			
	${}^3\Sigma_u^+$	$\delta_{3AB}({}^3\Sigma_u^+)$	+113.429	+102.780	+92.917	+100.002			
	Sum	δ_{3AB}	+34.364	+38.347	+40.306	+36.837			+40
$H_2^A+H_2^B$	${}^3\Sigma_g^+$	$\delta_{2AB}({}^3\Sigma_g^+)$	-0.443	-0.335	-0.254	-0.335			
	${}^3\Sigma_u^+$	$\delta_{2AB}({}^3\Sigma_u^+)$	+0.436	+0.377	+0.327	+0.369			
	${}^3\Pi_g$	$\delta_{2AB}({}^3\Pi_g)$	-0.106	-0.074	-0.052	-0.077			
	${}^3\Pi_u$	$\delta_{2AB}({}^3\Pi_u)$	+0.383	+0.273	+0.196	+0.279			
	${}^3\Delta_g$	$\delta_{2AB}({}^3\Delta_g)$	-0.358	-0.248	-0.172	-0.259			
	${}^3\Delta_u$	$\delta_{2AB}({}^3\Delta_u)$	+0.302	+0.222	+0.165	+0.225			
	Sum	δ_{2AB}	+0.213	+0.216	+0.208	+0.202			+3
H_2+H_3	Sum	$\delta_{2AB}+\delta_{3AB}$	+34.577	+38.563	+40.514	+37.039	+47.68	+47.49	
$H_1^A+H_1^B$	${}^1\Sigma_g^-$	$\delta_{1AB}({}^1\Sigma_g^-)$	-0.0019	-0.0012	-0.0007	-0.0013			
	${}^1\Sigma_u^-$	$\delta_{1AB}({}^1\Sigma_u^-)$	+0.0012	+0.0008	+0.0005	+0.0008			
	${}^1\Pi_g$	$\delta_{1AB}({}^1\Pi_g)$	-0.0497	-0.0381	-0.0289	-0.0375			
	${}^1\Pi_u$	$\delta_{1AB}({}^1\Pi_u)$	+0.5212	+0.3942	+0.2973	+0.3917			
	Sum	δ_{1AB}	+0.4709	+0.3557	+0.2682	+0.3538	+0.41	+0.47	<0.5
H_1^{AB}	${}^1\Sigma_g^+$	δ_{1AB}	-0.2508	-0.2859	-0.2908	-0.2544	+1.05	+1.61	-0.1 ^e
H_1	Sum	δ_{1AB}	+0.220	+0.070	-0.023	+0.099	+1.46	+2.08	
$H_1+H_2+H_3$	Sum Obs.	δ_{AB}	+34.797	+38.632	+40.492	+37.138	+49.14 42.7±0.7 ^f	+49.57	

^a For the unperturbed wave function, see reference 6. For the additional wave function, see Table I.

^b Averaged values over the zero-point vibration.

^c See reference 5. V.B. (valence bond) and M.O. (molecular orbital) indicate the wave function employed.

^d See reference 1.

^e Evaluated by using a simple HL (Heitler-London) wave function.

^f See reference 9.

of δ_{AB} over the zeroth vibrational state of the HD molecule, following the procedures given in reference 3. The results are given in Tables II and III. If we use for $\langle\delta_{3AB}\rangle_{00}$ the value given in Table III, and for the remaining contribution, $\langle\delta_{1AB}\rangle_{00}+\langle\delta_{2AB}\rangle_{00}$, the value obtained from Table II: (+0.301 cps), then $\langle\delta_{AB}\rangle_{00}$ becomes 35.217 cps, whereas the observed value is 42.7±0.7 cps.⁹ For comparison, we have given in Table II the results of Stephen⁵ and Ramsey.¹

DISCUSSIONS

As for the second-order terms, δ_{AB} , due to the set of additional wave functions of each symmetry property, we can prove the following qualitative properties (the proofs are given in the Appendix):

(A) Contributions from a set of functions with even symmetry, $\delta_{AB}(\text{even})$, are negative, whereas those from a set of functions with odd symmetry, $\delta_{AB}(\text{odd})$, are positive.

(B) At infinite internuclear distances, these two contributions are of equal magnitude and so their sum vanishes.

(C) The contribution from a set of functions with a given symmetry property increases numerically as the number of contributing functions increases; if the same unperturbed wave function is employed. The results

given in Tables II and III are in conformity with (A). If the James and Coolidge 11-term wave function can be taken as the exact wave function, we can conclude from (C) that the exact values of $\delta_{3AB}({}^3\Sigma_g^+)$ for each R_{AB} are smaller than the corresponding values given in Table III, and the exact values of $\delta_{3AB}({}^3\Sigma_u^+)$ for each R_{AB} are larger than those given in Table III. Thus we can see that the results for $\delta_{3AB}({}^3\Sigma_g^+)$ and $\delta_{3AB}({}^3\Sigma_u^+)$ are improved by using the James and Coolidge 11-term wave function instead of the unperturbed wave function given in reference 6. This fact is, however, not a logical consequence of the formalism, since, as pointed out by Rahman¹⁰ in the variational calculation of the polarizability, we cannot claim that the results are always improved by using a better unperturbed wave function. The fact that the results for the total sum δ_{AB} given in Table II are better than those in Table III may be due to a fortuitous cancellation of the errors in $\delta_{3AB}({}^3\Sigma_g^+)$ and $\delta_{3AB}({}^3\Sigma_u^+)$.

Now, considering that similar calculations of the various other quantities^{3,4} can yield values not so different from their respective observed values even when very simple forms are assumed for the additional wave function, it seems, then, not so surprising to expect a similar situation to hold in the present case.

⁹ T. F. Wimett, Phys. Rev. **91**, 476(A) (1953).

¹⁰ A. Rahman, Physica **19**, 145 and 377 (1953).

TABLE III. $\delta_{\delta AB}$ (in units of cps) calculated by using the James-Coolidge 11-term wave function ($\delta=0.75$)^a together with the ones given in Table I.

Perturbing Hamiltonian	Symmetry of additional function	Notation for each contribution	$\delta_{\delta AB}$ R_{AB} (au)				$\langle \delta_{\delta AB} \rangle_{00}^b$
			1.2	1.3	1.4	1.5	
$H_3^A + H_3^B$	${}^3\Sigma_g^+$	$\delta_{\delta AB}({}^3\Sigma_g^+)$	-101.600	-82.702	-67.666	-55.609	-66.058
	${}^3\Sigma_u^+$	$\delta_{\delta AB}({}^3\Sigma_u^+)$	+125.471	+113.726	+103.443	+94.205	+100.974
	Sum	$\delta_{\delta AB}$	+23.871	+31.024	+35.777	+38.596	+34.916

^a See reference 8.

^b Averaged values over the zero-point vibration.

Then we can see from Tables II and III the following points:

(a) As expected, the calculated values of δ_{AB} agree fairly well with the observed values.

(b) As a whole, the contributions from the even states are of the same order of magnitude as those from the corresponding odd states and so these contributions cancel each other appreciably. The tendency stated in (B), that is, $|\delta_{AB}(\text{even})|$ approaches the corresponding $|\delta_{AB}(\text{odd})|$, as R_{ab} increases, however, cannot always be seen in the neighborhood of the equilibrium internuclear distance. This tendency may be seen in the region of somewhat larger internuclear distances.

(c) As stated in the previous section, most of the contribution to δ_{AB} comes from $\delta_{\delta AB}$. This fact is in agreement with the results of Ramsey's estimate. The situation might be the same in Stephen's calculation, though only the sum of δ_{2AB} and δ_{3AB} is given in his paper.

(d) Ramsey estimated that $\delta_{2AB} \approx 3$ cps, but this value seems too large if the values calculated here give the right order of magnitude.

(e) The values of ${}^a\delta_{1AB}$ are found here to be negative. This fact means that the contribution to the integral $\langle \Phi_0 | \sum_j (\xi_{jA}\xi_{jB} + \eta_{jA}\eta_{jB} + \zeta_{jA}\zeta_{jB}) r_{jA}^{-3} r_{jB}^{-3} | \Phi_0 \rangle$ from the charge density of the electrons within the sphere of diameter AB is numerically larger than that from the remaining charge density. Ramsey obtained, by using a simple HL wave function, also a negative value for ${}^a\delta_{1AB}$, whereas Stephen obtained a positive one. The fact that Ramsey obtained a somewhat larger value than we do is reasonable, since the charge density between the two nuclei calculated by using the wave function employed here may be larger than that calculated by using the simple HL wave function. The fact that ${}^a\delta_{1AB}$ decreases as R_{AB} increases is also reasonable, considering that the volume of the above sphere increases with R_{AB} . Further, from the form of the above integrals together with the results given in Table II, we can expect that ${}^a\delta_{1AB}$ decreases with R_{AB} from a positive value at small values of R_{AB} to a negative value and reaches a minimum at a somewhat larger value than the equilibrium distance, and finally approaches zero as $R_{AB} \rightarrow \infty$.

(f) As for the values of ${}^b\delta_{1AB}$, the contribution due to the second-order effect of H_1 , our calculated value is

of the same order of magnitude as the one obtained by Stephen. These values fall within the region suggested by Ramsey.

(g) All the contributions from the second-order effect decrease numerically as R_{AB} increases.

(h) In order to obtain the value of δ_{AB} within an accuracy of a few percent, we must take into account the effect of averaging over the zero-point vibration.

Further, we note here that no appreciable correlation can be found between the contributions from each symmetry state and the lowest term values belonging to the corresponding symmetry states. This is similar to what is found in other cases.² For example, the polarizabilities of the O₂ molecule¹¹ could not be explained by taking into account a few low-lying states.

The final result for $\langle \delta_{AB} \rangle_{00}$ obtained in the previous section is 35.217 cps as compared to the observed value of 42.7 ± 0.7 cps,⁹ and the agreement is satisfactory, considering that we took into account only a small number of additional perturbative functions and that the contributions from the even states and the odd states cancel appreciably.

ACKNOWLEDGMENTS

The author is much obliged to Professor J. C. Slater for the opportunity to carry out this work at the Massachusetts Institute of Technology and for his valuable advice. Also he has the pleasure to express his cordial gratitude to Professor M. Kotani for his kind and continuous encouragement, and to Dr. A. J. Freeman for his helpful comments on the original manuscript.

APPENDIX

I. Proof of (A)

In the first place, we note that

$$H^{B\xi}(P_1, P_2) = H^{A\xi}(IP_1, IP_2),$$

$$(\xi \text{ represents } \xi, \eta, \text{ or } \zeta), \quad (\text{A.1})$$

where P_i ($i=1, 2$) means the position of the electron i and I means the inversion operator with respect to the midpoint of the two nuclei. Then we can find the follow-

¹¹ Kotani, Mizuno, Kayama, and Ishiguro, J. Phys. Soc. Japan 12, 707 (1957).

ing relations:

$$H_{k_i}^{A\xi} = \{\pm\} H_{k_i}^{B\xi}, \quad (\xi \text{ represents } \xi, \eta, \text{ or } \zeta). \quad (\text{A.2})$$

Here and in what follows, we assume that we choose a plus sign in $\{\pm\}$ when $\varphi_k \Theta_k$ is of even symmetry and a minus sign when this is of odd symmetry. Hence, from (12), we have

$$a_{k\xi} = \{\pm\} b_{k\xi}, \quad (\xi \text{ represents } \xi, \eta, \text{ or } \zeta). \quad (\text{A.3})$$

Then, from Eq. (14), we can see that

$$\bar{\delta}_{AA}^{\xi\xi} = \{\langle \Phi_0 | H^{A\xi} | \Phi_{\xi, e} \rangle + \langle \Phi_0 | H^{A\xi} | \Phi_{\xi, o} \rangle\}, \quad (\text{A.4.1})$$

$$\bar{\delta}_{AB}^{\xi\xi} = 2\{\langle \Phi_0 | H^{A\xi} | \Phi_{\xi, e} \rangle - \langle \Phi_0 | H^{A\xi} | \Phi_{\xi, o} \rangle\}, \quad (\text{A.4.2})$$

where

$$\Phi_{\xi, e} = \sum_{k(\text{even})} a_{k\xi} \varphi_k \Theta_k, \quad (\text{A.5.1})$$

$$\Phi_{\xi, o} = \sum_{k(\text{odd})} a_{k\xi} \varphi_k \Theta_k, \quad (\text{A.5.2})$$

and $\sum_{k(\text{even})}$ and $\sum_{k(\text{odd})}$ mean the summation over the functional space with even symmetry and that with odd symmetry, respectively. Further, from Eqs. (12.1) and (12.2), taking into consideration the fact that E_0 is the eigenvalue of the lowest energy level, we can see that

$$\langle \Phi_0 | H^{A\xi} | \Phi_{\xi} \rangle = -\langle \Phi_{\xi} | H^0 - E_0 | \Phi_{\xi} \rangle < 0, \quad (\text{A.6})$$

where Φ_{ξ} stands for $\Phi_{\xi, e}$ and $\Phi_{\xi, o}$. This leads directly to the statement (A). This situation can be explained also on the basis of perturbation theory. According to this theory, we can see that

$$\begin{aligned} \delta_{AB} &= -\frac{\gamma_A \gamma_B}{3h} \sum_{\xi, n} \frac{1}{E_n - E_0} \\ &\quad \times \{\langle \Phi_0 | H^{A\xi} | \Phi_n \rangle \langle \Phi_n | H^{B\xi} | \Phi_0 \rangle + \text{c.c.}\}. \quad (\text{A.7}) \end{aligned}$$

Then we can prove (A) straightforwardly, since $E_n > E_0$ and the quantities in the brackets are positive or negative if Φ_n is of an even symmetry or of an odd symmetry.

II. Proof of (B)

In the limit of infinite nuclear separation, Φ_n in (A.7) may be composed to a good approximation from

the atomic orbitals of the ground state of one atom ϕ_{N^0} ($N=A$ or B) and that of the excited state of the other atom $\phi_{N'^n}$ ($N'=B$ or A). Further, we can construct from these orbitals the total wave function with even symmetry, $\Phi_{n, e}$, as well as that with odd symmetry, $\Phi_{n, o}$. Since the total energy E_n is the same for these two wave functions at $R_{AB} = \infty$, whereas the numerator of (A.7) is numerically equal and is of the opposite sign, as stated in (A), we can conclude that the sum of contributions from these two states vanishes as $R_{AB} \rightarrow \infty$.

The situation can be explained also in our formalism. For this purpose, we use the aforementioned $\Phi_{n, e}$ and $\Phi_{n, o}$ as $\varphi_k \Theta_k$ in Eq. (6) and denote their coefficients as $a_{n, e, \xi}$, $a_{n, o, \xi}$, $b_{n, e, \xi}$, $b_{n, o, \xi}$, \dots . Then we can see from Eq. (12) the relations like

$$\begin{aligned} \langle \Phi_{n, e} | H^{A\xi} | \theta_i \Theta_0 \rangle &= \langle \Phi_{n, o} | H^{A\xi} | \theta_i \Theta_0 \rangle, \\ a_{n, e, \xi} &= a_{n, o, \xi}, \quad (\text{B.1.1}) \end{aligned}$$

$$\langle \Phi_{n, e} | H^{B\xi} | \theta_i \Theta_0 \rangle = -\langle \Phi_{n, o} | H^{B\xi} | \theta_i \Theta_0 \rangle,$$

$$b_{n, e, \xi} = -b_{n, o, \xi}, \quad (\xi \text{ represents } \xi, \eta, \text{ or } \zeta). \quad (\text{B.1.2})$$

Hence we can conclude that $\bar{\delta}_{AB}^{\xi\xi}$ vanishes [see Eq. (A.4)]. Further, from (6) and (B.1), it is shown that ϕ_{B^n} ($n \neq 0$) can be eliminated from the second sum of (6) and ϕ_{A^n} ($n \neq 0$) can be eliminated from the third sum of (6). This fact is as it should be in the limit as $R_{AB} \rightarrow \infty$, since the nuclear moment of one nucleus may not affect the charge density in the neighborhood of the other nucleus.

III. Proof of (C)

The system of equations (12.1) and (12.2), determining the coefficients $a_{k\xi}$ is found to be nothing more than the condition to minimize the parts of the energy expression with the factors $\gamma_A^2 \langle x_0 | I_{A\xi}^2 | x_0 \rangle$ and $\gamma_B^2 \langle x_0 | I_{B\xi}^2 | x_0 \rangle$, respectively. Then $\langle \Phi_0 | H^{A\xi} | \Phi_{\xi, e} \rangle$ and $\langle \Phi_0 | H^{A\xi} | \Phi_{\xi, o} \rangle$ [see Eq. (A.4)] must decrease as we employ a more flexible additional wave function, under the condition of assuming the same Φ_0 . Hence, from Eq. (A.4.2), we can conclude (C). We mention, further, that $a_{k\xi}$, for example, is determined by the form of the operators $H^{A\xi}$ only, besides Φ_0 and the $\varphi_k \Theta_k$. A similar situation can be seen easily in the perturbation theory.