PHYSICAL REVIEW VOLUME 115, NUMBER 4 AUGUST 15, 1959

Electric and Magnetic Properties of the Hydrogen Molecule*†

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(Received January 9, 1959)

The hydrogen molecule ground state has been studied for a long time by valence theorists. Comparison with experiment has been limited to the energy, bond distance, vibration frequency, and the electric and magnetic polarizabilities. Recent radio-frequency experiments on hydrogen have yielded new quantities, the nuclear magnetic shielding constant, the spin-spin coupling constant, and the electric field gradient at the nucleus. In this paper, variation methods are described for the calculation of the new types of polarizability. These methods can be applied to more complex molecules and appear to open new possibilities for the semiquantitative interpretation of the results of high-resolution nuclear magnetic resonance. An extensive comparison is made between the experimental quantities and theoretical values using various wave functions. The most important factor affecting the accuracy of the charge density is the use of an effective nuclear charge.

A VAST literature exists on the ground state of the hydrogen molecule. Since the definitive work of James and Coolidge[1] appeared, the chief task has been to develop reasonably accurate but more convenient wave functions and to extract physical meaning from the more complicated ones. Inasmuch as the true wave function is not known, it has been customary to test approximations by comparison of the experimental and calculated bond energies. The experiments on molecular hydrogen beams in recent years by Ramsey[2] and his collaborators have made it possible to adopt a new viewpoint. In this paper, the quality of various wave functions is treated by considering the interactions which arise from external fields and from the nuclear multipole moments.

We have neglected the effects of molecular vibrations and rotations. Vibrational motion would lead to corrections to the quantities calculated in this paper. Rotational motion produces other physically measurable quantities such as a rotational magnetic moment of the molecule and a magnetic field at each of the nuclei. These[2] are simply related to the paramagnetic parts of the susceptibility and nuclear magnetic shielding constants, respectively.

A general Hamiltonian[3] for a rigid molecule in the presence of static external magnetic and electric fields and electric field gradients is given in Eq. (1):

$$\begin{aligned}\mathcal{H}=\sum_k \frac{[\mathbf{p}_k+(e/c)\mathbf{A}(\mathbf{r}_k)]^2}{2m}+\sum_{k<k'}\frac{e^2}{r_{kk'}}+\sum_{N<N'}\frac{Z_N Z_{N'}e^2}{R_{NN'}}\\ -\sum_k\sum_N \frac{Z_N e^2}{r_{Nk}}+Q_{\text{mol}}\cdot\nabla\mathcal{E}_{\text{ext}}+\sum_k e\mathbf{r}_k\cdot\boldsymbol{\varepsilon}_{\text{ext}}\\ -\sum_N e\mathbf{R}_N Z_N\cdot\boldsymbol{\varepsilon}_{\text{ext}}-\sum_N g_N\beta_{\text{nuc}}\mathbf{I}_N\cdot\nabla\times\mathbf{A}(\mathbf{R}_N)\\ +\sum_N Q_N\cdot(\nabla\mathcal{E})_{\text{int at }N}-\sum_k g\beta\mathbf{S}_k\cdot\nabla\times\mathbf{A}(\mathbf{r}_k),\end{aligned}\quad(1)$$

where

$$\mathbf{A}=\mathbf{A}_{\text{ext}}+\sum_N \mathbf{A}_{\text{nuc}}{}^{(N)}=\tfrac{1}{2}\mathbf{H}\times\mathbf{r}_k+\sum_N\frac{\boldsymbol{\mu}_N\times\mathbf{r}_{kN}}{r_{kN}{}^3}.$$

Let $\mathcal{H}_0$ be the Hamiltonian in which all nuclear moments and external fields have been dropped. The energies associated with $\mathcal{H}-\mathcal{H}_0$ will be negligible in magnitude because of the small size of external fields compared to internal fields ($\mathcal{E}a_0^2/e\ \ 10^{-5}$), because of the small size of the nucleus compared to the atom ($Q/a_0^2\sim 10^{-9}$) and because of the smallness of the fine structure constant ($\alpha=e^2/\hbar c=1/137$).

We shall try to see how this feeble part of the Hamiltonian can be used to elucidate the charge distribution associated with the ground-state eigenfunction Ψ_0 of $\mathcal{H}_0$. Some of the feeble interactions contribute in the first order, i.e., their experimental magnitudes are expectation values of various functions of the electron and nuclear coordinates. These expectation values will be compared for the different trial wave functions. Some interactions contribute only in the second order. The effects of polarizing the various zero-order wave functions will be compared.

I. VARIATION TREATMENT OF POLARIZATIONS

A. General Description of the Method

In every case of polarization, one has the following situation. There is a Hamiltonian of the form

$$\mathcal{H}=\mathcal{H}_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)+\boldsymbol{\nu}\cdot\boldsymbol{\mathcal{H}}_1(\nu),\quad(2)$$

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* Financial support for this work was given by the U. S. Atomic Energy Commission and the National Science Foundation.

† Portions of this work have earlier been briefly reported: T. P. Das, Bull. Am. Phys. Soc. 1, 215 (1956); T. P. Das and R. Bersohn, Phys. Rev. 104, 849 (1956).

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[2] N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, 1956).

[3] A. Abragam, Suppl. Nuovo cimento 6, 1015 (1957).

where $\boldsymbol{\varepsilon}$ and $\mathbf{v}$ are small vectors (one of which may, in fact, be zero). The wave function and the energy are developed in power series of the small vector components:

$$\Psi=\Psi_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu), \tag{3}$$

$$E=E_0+\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\{E_{\kappa\lambda}(\epsilon)\epsilon_\kappa\epsilon_\lambda+E_{\kappa\lambda}(\epsilon\nu)\epsilon_\kappa\nu_\lambda +E_{\kappa\lambda}(\nu)\nu_\kappa\nu_\lambda\}. \tag{4}$$

Note that the first-order terms in the energy are zero. The notation $\boldsymbol{\psi}_1(\epsilon)$ means that $\boldsymbol{\psi}_1$ is a vector function as well as the part of an eigenvector $\boldsymbol{\Psi}$ produced in the first order by a perturbation associated with the vector $\boldsymbol{\varepsilon}$. The terms $E_{\kappa\lambda}(\epsilon)$, $E_{\kappa\lambda}(\nu)$, and $E_{\kappa\lambda}(\epsilon\nu)$ are (aside from numerical factors) just the polarizability tensors. These include the electrical polarizability tensor $\alpha_{\kappa\lambda}$, the paramagnetic part of the magnetic susceptibility tensor $\chi_{\kappa\lambda}$ [tensor of the form $E_{\kappa\lambda}(\epsilon)$], and also the paramagnetic part of the magnetic shielding tensor at nucleus l, $\sigma_{\kappa\lambda}{}^{(l)}$, and the spin-spin interaction tensor $J_{\kappa\lambda}{}^{(kl)}$ between nuclei k and l [tensor of the form $E_{\kappa\lambda}(\epsilon\nu)$]. By substitution of the power series developments into the Schrödinger equation, one obtains an equation for $\boldsymbol{\psi}_1(\epsilon)$,

$$(\mathcal{H}_0-E_0)\boldsymbol{\psi}_1(\epsilon)=-\boldsymbol{\mathcal{H}}_1(\epsilon)\Psi_0. \tag{5}$$

The usual solution to this equation is the familiar expression

$$\boldsymbol{\psi}_1(\epsilon)=\sum_{n\neq0}\mathbf{c}_n(\epsilon)\Psi_n, \tag{6}$$

where the Ψ_n are the eigenfunctions of $\mathcal{H}_0$. The result for the energy, and thus for the polarizability tensors, is

$$E=E_0+\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\epsilon_\kappa\epsilon_\lambda\frac{\sum_{n\neq0}\langle\Psi_0|\mathcal{H}_{1\kappa}|\Psi_n\rangle\langle\Psi_n|\mathcal{H}_{1\lambda}|\Psi_0\rangle}{E_0-E_n}. \tag{7}$$

This is the usual result[4] which is excellent for physical understanding but almost useless for numerical computation inasmuch as the excited functions Ψ_n and excited levels E_n are unknown.

There are at least two other ways to solve Eq. (5) and obtain an expansion for the energy. One is to solve, directly, the inhomogeneous differential equation by numerical methods. This is ideal in atomic problems where Eq. (5) often reduces to a differential equation in the radial coordinate alone.[5] This does not happen in the molecular case and one is left with the possibility of using a variational wave function. The total energy in the general two-vector case which is to be minimized can be obtained from its definition

$$E=\frac{\langle\Psi_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)|\mathcal{H}_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)|\Psi_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle}{\langle\Psi_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)|\Psi_0+\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle}, \tag{8}$$

which reduces (if one assumes that $\mathcal{H}_0\Psi_0$ is orthogonal to ψ_1 and neglects higher than quadratic terms) to

$$\begin{aligned}E=E_0&+2\langle\Psi_0|\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)|\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\rangle\\&+\langle\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)|\mathcal{H}_0-E_0|\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\rangle+2\langle\Psi_0|\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle\\&+\langle\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)|\mathcal{H}_0-E_0|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle+2\langle\Psi_0|\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle\\&+2\langle\Psi_0|\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)|\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\rangle\\&+2\langle\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)|\mathcal{H}_0-E_0|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle.\end{aligned} \tag{9}$$

On allowing the functions $\boldsymbol{\psi}_1(\epsilon)$ and $\boldsymbol{\psi}_1(\nu)$ to be varied by the addition of small arbitrary vectors $\delta\boldsymbol{\psi}_1(\epsilon)$ and $\delta\boldsymbol{\psi}_1(\nu)$, one sees that the variation δE in E is

$$\begin{aligned}\delta E=2\langle&\boldsymbol{\varepsilon}\cdot\delta\boldsymbol{\psi}_1(\epsilon)+\mathbf{v}\cdot\delta\boldsymbol{\psi}_1(\nu)\\&\times|\{\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)\Psi_0+(\mathcal{H}_0-E_0)\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\}\\&+\{\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)\Psi_0+(\mathcal{H}_0-E_0)\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\}\rangle.\end{aligned} \tag{10}$$

To hold the entire second-order energy stationary, it is necessary and sufficient that the contents of the curly brackets vanish, i.e., that the first-order Schrödinger equations be satisfied. There are two approaches by which one could simplify the calculation. If one is interested in the energy terms of orders ϵ^2 and $\epsilon\nu$, it is sufficient to vary the terms of order ϵ^2 alone[6] with respect to variations in $\boldsymbol{\psi}_1(\epsilon)$. On the other hand, if one is interested only in energy terms of the order $\epsilon\nu$, then one may minimize energy terms of this order alone. To prove the first statement, suppose that Eq. (5) for $\boldsymbol{\psi}_1(\epsilon)$ is satisfied. The energy then becomes

$$\begin{aligned}E=E_0&+\langle\Psi_0|\boldsymbol{\varepsilon}\cdot\boldsymbol{\mathcal{H}}_1(\epsilon)|\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\rangle+2\langle\Psi_0|\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle\\&+\langle\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)|\mathcal{H}_0-E_0|\mathbf{v}\cdot\boldsymbol{\psi}_1(\nu)\rangle\\&+2\langle\Psi_0|\mathbf{v}\cdot\boldsymbol{\mathcal{H}}_1(\nu)|\boldsymbol{\varepsilon}\cdot\boldsymbol{\psi}_1(\epsilon)\rangle.\end{aligned} \tag{11}$$

The part of the energy of order ν^2 is not stationary but the parts of the energy of order ϵ^2 and $\epsilon\nu$ depend only on $\boldsymbol{\psi}_1(\epsilon)$ and are therefore stationary.

Besides showing that the second-order energy is stationary when the first-order Schrödinger equation is satisfied, it is instructive to show that the energy is minimized. The second-order variation in the second-order energy using Eq. (9) due to changes $\delta\boldsymbol{\psi}_1(\epsilon)$ and

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[4] The results on the non-nuclear polarizations are in J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, Oxford, 1932), pp. 189, 275, and on the nuclear polarizationsin reference 2, pp. 163, 207.

[5] R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

[6] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); T. P. Das and T. Ghose, J. Chem. Phys. **31**, 42 (1959).

$\delta\psi_1(\nu)$ is

$$\delta^2E=\langle\boldsymbol{\varepsilon}\cdot\delta\psi_1(\epsilon)+\boldsymbol{\nu}\cdot\delta\psi_1(\nu)\,|\,\mathcal{H}_0-E_0\,|\,\boldsymbol{\varepsilon}\cdot\delta\psi_1(\epsilon)+\boldsymbol{\nu}\cdot\delta\psi_1(\nu)\rangle\geqslant 0, \quad (12)$$

whereas substituting the first-order Schrödinger equation in Eq. (9), one finds

$$E-E_0=-\langle\boldsymbol{\varepsilon}\cdot\psi_1(\epsilon)+\boldsymbol{\nu}\cdot\psi_1(\nu)\,|\,\mathcal{H}_0-E_0\,|\,\boldsymbol{\varepsilon}\cdot\psi_1(\epsilon)+\boldsymbol{\nu}\cdot\psi_1(\nu)\rangle\leqslant 0. \quad (13)$$

The total second-order energy is negative but its second variation is positive showing that the approximate second-order energy is always greater than its value obtained by correctly solving the first-order Schrödinger equation. The inequalities of Eqs. (12) and (13) are valid if Ψ_0 is only an approximation to the eigenfunction corresponding to the lowest eigenvalue. (They would fail only in the absurd circumstance that Ψ, or $\delta\Psi_1$ were a better approximation than Ψ_0 to the lowest eigenfunction.)

B. Representation of Ψ as a Multiple of Ψ_0

Particularly simple expressions and moreover rapidly convergent energies result from using a wave function of the form

$$\Psi=[1+\boldsymbol{\varepsilon}\cdot\mathbf{P}(\epsilon)+\boldsymbol{\nu}\cdot\mathbf{P}(\nu)]\Psi_0. \quad (14)$$

Sternheimer has shown in several papers, e.g.,reference 5, that for many polarization problems involving hydrogenic wave functions, the exact first-order perturbation function involves a very simple **P** function. The essential discovery is that the **P** function can be fairly simple and yet provide satisfactory energies. The polarization phenomena can then be related to expectation values of the coordinate operators over the ground state Ψ_0. More specifically, by partial integrations, the energy assumes the form

$$\begin{aligned}E=E_0+\sum_{k=1}^{3}\sum_{\lambda=1}^{3}\epsilon_\kappa\epsilon_\lambda\Big\{&\langle\Psi_0|\mathcal{H}_{1\kappa}(\epsilon)P_\lambda(\epsilon)+P_\kappa{}^*(\epsilon)\mathcal{H}_{1\lambda}(\epsilon)|\Psi_0\rangle\\&+\frac{\hbar^2}{2m}\langle\Psi_0|\sum_k\nabla_kP_\kappa{}^*(\epsilon)\cdot\nabla_kP_\lambda(\epsilon)|\Psi_0\rangle\Big\}\\+2\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\epsilon_\kappa\nu_\lambda\Big\{&\langle\Psi_0|\mathcal{H}_{1\kappa}(\epsilon)P_\lambda(\nu)+P_\kappa{}^*(\epsilon)\mathcal{H}_{1\lambda}(\nu)|\Psi_0\rangle\\&+\frac{\hbar^2}{2m}\langle\Psi_0|\sum_k\nabla_kP_\kappa{}^*(\epsilon)\cdot\nabla_kP_\lambda(\nu)|\Psi_0\rangle\Big\}\\&+\nu^2\text{ terms.}\end{aligned} \quad (15)$$

Moreover for functions $\psi_1(\epsilon)$ and $\psi_1(\nu)$ which satisfy equations of the form (5), the energy further simplifies to

$$\begin{aligned}E=E_0+\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}[&\epsilon_\kappa\epsilon_\lambda\langle\Psi_0|\mathcal{H}_{1\kappa}(\epsilon)P_\lambda(\epsilon)|\Psi_0\rangle\\&+\epsilon_\kappa\nu_\lambda\langle\Psi_0|\mathcal{H}_{1\kappa}(\epsilon)P_\lambda(\nu)+P_\kappa{}^*(\epsilon)\mathcal{H}_{1\lambda}(\nu)|\Psi_0\rangle\\&+\nu_\kappa\nu_\lambda\langle\Psi_0|\mathcal{H}_{1\kappa}(\nu)P_\lambda(\nu)|\Psi_0\rangle].\end{aligned} \quad (16)$$

In this way, the feeble polarization terms in the Hamiltonian are made to serve their avowed purpose more directly, that is, to give information about the charge density itself. With a molecule containing more than two electrons, different functions $\mathbf{P}(\epsilon)$ would have to be used for the different electron states and the procedure would have to be generalized.[6]

II. EXPECTATION VALUES OVER THE GROUND-STATE CHARGE DISTRIBUTION

To test the various approximate wave functions, a mathematical experiment is performed. This consists in computing with each wave function or using literature values for (1) the second moments of the electron distribution, (2) the expectation values of inverse functions of the electron nuclear separation, and (3) the expectation values of functions of the coordinates of two electrons.

A. Wave Functions Used for Comparison

The wave functions used in the "experiment" were a set of nine valence bond and molecular orbital functions. In each of the tables to follow the first five functions are of the valence bond type and the next four of the molecular orbital type. Naturally, the more refined members of each type resemble each other. The Hirschfelder-Linnett[7] function has the form

$$\begin{aligned}\Psi/N=a(1)b(2)[&1+\alpha Z^2\{x_A(1)x_B(2)+y_A(1)y_B(2)\}\\&+\beta Z^2z_A(1)z_B(2)]+a(2)b(1)\\&\times[1+\alpha Z^2\{x_A(2)x_B(1)+y_A(2)y_B(1)\}\\&+\beta Z^2z_A(2)z_B(1)]+\gamma[a(1)a(2)+b(1)b(2)],\end{aligned}$$

where a and b are $1s$ functions with effective nuclear charge Z, centered on nuclei A and B, respectively. If one sets $\alpha=\gamma=0$, a function resembling the Rosen[8] function results; if one sets $\alpha=\beta=0$, the Weinbaum[9] function is obtained. If $\alpha=\beta=\gamma=0$, one has the Wang[10] function. The latter becomes the original Heitler-London[11] function if $Z=1$. In each case, Z and the normalization constant N have different numerical values. The Wallis[12] function has the form

$$\begin{aligned}\Psi/N=a^A(1)b^B(2)+b^B(1)a^A(2)+b^A(1)a^B(2)+a^B(1)b^A(2)\\+\lambda[a^A(1)a^B(2)+b^A(1)b^B(2)\\+a^B(1)a^A(2)+b^B(1)b^A(2)],\end{aligned}$$

where a^A and a^B are $1s$ functions with effective nuclear charge Z_A and Z_B centered on nucleus a. If the parameter λ is unity, the resulting function is called the Wallis open shell function (equivalent to configuration interaction, C.I.); if λ is chosen to minimize the binding energy, it is called the Wallis limited ionic open

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[7] J. Hirschfelder and W. Linnett, J. Chem. Phys. **18**, 130 (1950).
[8] N. Rosen, Phys. Rev. **38**, 2099 (1931).
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[12] R. F. Wallis, J. Chem. Phys. **23**, 1256 (1955).

TABLE I. Expectation values of quadratic functions of the coordinates for $R=1.40a_0$ (units of a_0^2).

Wave function	$\langle x_c^2\rangle = \langle y_c^2\rangle$	$\langle z_c^2\rangle$	$\langle \frac{1}{2}(3z_c^2-r_c^2)\rangle = \langle z_c^2-x_c^2\rangle$	Binding energy $=-\langle\mathcal{H}_0\rangle$ -27.06 ev
Heitler-London	1.0371	1.385	0.348	3.14
Wang	0.767	1.131	0.364	3.76
Weinbaum	0.738	1.082	0.344	4.00
Rosen	0.742	0.964	0.222	4.02
Hirschfelder-Linnett	0.744	1.070	0.326	4.25
Coulson (unshielded)	1.044	1.367	0.323	2.68
Coulson (shielded)	0.742	1.073	0.332	3.47
Wallis (C.I.)	0.816	1.147	0.331	3.57
Wallis (limited ionic)	0.761	1.108	0.347	4.08
Nordsieck	0.745	1.009	0.264	4.03
James-Coolidge 5-term			0.269 (0.278)	4.51
Newell	0.731	1.002	0.271	4.53
Ramsey (exp.)	0.7663	1.0604	0.2941	4.74

shell function. Letting $\lambda=1$ and $Z_A=Z_B$ produces the shielded molecular orbital function of Coulson[13]; and if $\lambda=Z_A=Z_B=1$, one has the Coulson unshielded function.

B. Second Moments of the Electron Distribution

Table I contains expectation values of quadratic functions of the coordinates obtained at the equilibrium internuclear distance $R=1.4a_0$, where a_0 is the Bohr radius. To compare with experiment an average of each quantity should be taken over the ground vibrational state of the molecule. This has not been done to save labor, but the vibrational correction is usually[14] small compared to the difference between the calculated and experimental values. The task of evaluating the second moments of the various H_2 wave functions was begun by James and Coolidge[15] and its utility was pointed out by Karplus.[14]

For H_2 we are in the unique position at present of having accurate experimental[2] values of $\langle x_c^2\rangle$ and $\langle z_c^2\rangle$. Table I shows that to obtain reasonably accurate (5–10% error) second moments of the charge distribution, one only needs to have a wave function with a scale factor Z. The only poor expectation values are those for which $Z=1$. As soon as $Z\sim 1.2$, the charge distribution is sufficiently contracted to give the right "size".[14] The Rosen function is an exception insofar as $\langle z_c^2\rangle$ is concerned. This is because in the process of hybridization, the density in the internuclear region is increased too much at the expense of the density at the ends of the molecule. The lateral spread of the charge distribution is not much disturbed.

TABLE II. Expectation values of inverse functions of the coordinates at $R=1.4a_0$ (in units of a_0).

Function	$\langle 1/r\rangle$	$\langle z/r^3\rangle$	$\langle (3z^2-r^2)/r^5\rangle$	$\langle \delta(r)\rangle$	$\langle (3z^2-r^2)/r^3\rangle$
Heitler-London	0.798	0.159	0.1224	0.145	0.217
Wang	0.895	0.202	0.1634	0.224	0.252
Weinbaum	0.908	0.215	0.1724	0.231	0.257
Rosen	0.915	0.245	0.1694	0.216	0.242
Hirschfelder-Linnett	0.926	0.225	0.1714	0.230	0.247
Coulson (unshielded)	0.797	0.153	0.1227	0.126	0.203
Coulson (shielded)	0.932	0.219	0.1744	0.199	0.255
Wallis (C.I.)	0.920	0.208	0.1788	0.241	0.255
Wallis (limited ionic)	0.917	0.263	0.1768	0.206	0.325
Best theoretical value	0.915[a]	0.255	0.1782[a]	0.220[a]	···

[a] Value computed by G. F. Newell [Phys. Rev. 78, 711 (1950); 80, 476 (1950)].

The quadrupole moment is a more sensitive quantity which is not given really well until the Nordsieck[16] approach is used. He replaces the simple exponential

$$e^{-Zr_A}=e^{-(Z/2)(r_A+r_B)}e^{-(Z/2)(r_A-r_B)},$$

by a generalized function in which the Z's in the two exponentials are different. In effect, the parameter Z is no longer isotropic and the scale factors for the lateral and longitudinal charge distributions become at least partially decoupled. The value in parentheses after the James-Coolidge five-term function is that obtained by averaging over the ground vibrational state. The last three values of the quadrupole moment are thus closer to experiment than might appear. In conclusion then, judging from its second moments, the charge density in the outer regions of the molecule is adequately represented by almost all one-parameter wave functions and is well represented by Nordsieck's two-parameter function.

C. Expectation Values of Inverse Functions of the Electron-Nuclear Separation

We consider first the expectation values of the potential, electric field, and electric field gradient produced by an electron at one of the nuclei. The potential seen by a nucleus is just the potential due to the other nucleus e/R plus the potential due to the two electrons $-e/r_1-e/r_2$. The figures in the first column of Table II show that $\langle 1/r\rangle$ is given to about 2–3% accuracy with any function possessing an effective nuclear charge.

In contrast to $1/r$, of all the operators considered here, the disagreement between observed and calculated expectation values is worst for z/r^3, errors of 15–25% being common. The electric field seen by a nucleus when it is at equilibrium must, by definition, be zero so that the electric field from each of the two electrons is just $-\frac{1}{2}$ the field originating from the other nucleus, i.e., $-\frac{1}{2}e/R^2=(-e)(0.255)a_0^{-2}$. The deviation of the numbers in the second column of Table II from 0.255 is a measure of the electric field seen by the nucleus. A desirable physical requirement is that the energy minimum with respect to R be self-consistent, i.e., that the electric field be zero at the nucleus for equilibrium value

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[13] C. A. Coulson, Trans. Faraday Soc. 33, 1479 (1937).
[14] M. Karplus, J. Chem. Phys. 25, 605 (1956).
[15] H. James and A. S. Coolidge, Astrophys. J. 87, 447 (1938).
[16] A. Nordsieck, Phys. Rev. 58, 310 (1940).

TABLE III. Expectation values of two-electron operators for $R=1.4a_0$ (units of a_0).

Wave function	$\langle z_c(1)z_c(2)\rangle$	$\langle x_c(1)x_c(2)\rangle$	$\langle 1/r_{12}\rangle$	$\langle\delta(\mathbf{r}_A(1))\delta(\mathbf{r}_B(2))\rangle$	$\dfrac{\langle\delta(\mathbf{r}_A(1))\delta(\mathbf{r}_B(2))\rangle}{\langle\delta(\mathbf{r}_A(1))\rangle\langle\delta(\mathbf{r}_B(2))\rangle}-1$
Heitler-London	−0.313	0	0.529	0.0364	0.719
Wang	−0.333	0	0.593	0.0932	0.861
Weinbaum	−0.203	0	0.617	0.0840	0.569
Rosen	−0.177	0	0.649	0.0960	1.057
Hirschfelder-Linnett	−0.225	−0.041	0.622	0.0779	0.473
Coulson (unshielded)	−0	0	0.566	0.0158	0.000
Coulson (shielded)	0	0	0.656	0.0527	0.000
Wallis (C.I.)	0	0	0.702	0.0522	−0.101
Wallis (limited ionic)	−0.209	0	0.652	0.1145	0.399
Newell	...	...	0.611	0.0561	0.158
James-Coolidge	...	...	...	0.0600	0.206[a]

[a] Approximate because approximate value of density was used.

of R. This is the Hellman-Feynman theorem,[17] equivalent to the condition $\int(\partial\psi/\partial R)\mathcal{H}\psi d\tau_1 d\tau_2=0$ which is, however, difficult to apply in practice.[18]

The derivative of the electric field at a nucleus consists of two parts, one coming from the other nucleus $(+e)(2/R^3)=(+e)(0.7289)a_0^{-3}$ and the other coming from the two electrons. The field gradient from each electron is, in fact, about one-fourth of the field gradient from the other nucleus and of opposite sign. In contrast to the electric field, it is easily possible to obtain a wave function which gives a value of the field gradient accurate to 5%.

The charge density in the neighborhood of the nucleus would appear to be in error as far as the electric field is concerned, but not with respect to the potential or field gradient. This paradox is resolved by considering $\langle\delta(\mathbf{r})\rangle$, that is, one half the charge density at the nucleus. This quantity is given as accurately as the field gradient. A geometrical picture will show in what way the charge density is in error. Imagine that a small sphere of radius δ is constructed around each nucleus. At each small distance, $\delta\mathbf{r}$ ($|\delta\mathbf{r}|\leq\delta$) to the right of nucleus B (and to the left of nucleus A) some charge is removed and placed at the point $-\delta\mathbf{r}$. This imaginary operation alters neither the charge density at the nucleus nor the expectation values of even functions of x, y, or z. However, $\langle z/r^3\rangle$ would increase by a term of order δ^2 whereas $\langle z_c^2\rangle$ would decrease by a term of order δ^5. A substantial increase in the electric field with an accompanying very small decrease in $\langle z_c^2\rangle$ would be perfectly in accord with experiment. Analytically, this operation corresponds to a hybridization in which the p function has an independent and quite large effective nuclear charge. These considerations suggest that an excellent charge distribution and presumably a fair energy would be obtained by using a wave function with three variation parameters: two effective nuclear charges for the s, p functions and the ratio of the amplitudes of the s and p functions.

The values for the field gradient at the nucleus due to the electrons vary remarkably little among the different wave functions. The better functions do tend to concentrate the electrons along the bond axis so that there is a slight tendency for the electronic contribution to the field gradient to rise as the binding energy increases. The field gradient when calculated from the James-Coolidge function might well be a few percent higher than Newell's value; the calculated deuteron quadrupole moment would then increase because the *total* calculated field gradient would decrease.

The quantity $\langle(3z^2-r^2)/r^3\rangle$, which is proportional to the anisotropy of the magnetic shielding of the proton, is tabulated for use in the future when this anisotropy can be measured. Its values over the different wave functions are almost as steady as $\langle 1/r\rangle$.

D. Expectation Values of Two Electron Operators

In Secs. B and C of part II, the one-electron density $\rho(\mathbf{r}_1)$ associated with various trial wave functions for H_2 has been inferred from expectation values of one-electron operators. In this section we infer some properties of the pair distribution function $\rho(\mathbf{r}_1,\mathbf{r}_2)$ from the expectation values of two-electron operators.

Table III presents four different indices of electron correlation. The interelectron interaction energy $\langle r_{12}^{-1}\rangle$ is in a different class from the quantities $\langle z_c(1)z_c(2)\rangle$, $\langle x_c(1)x_c(2)\rangle$, and $\langle\delta(\mathbf{r}_A(1))\delta(\mathbf{r}_B(2))\rangle-\langle\delta(\mathbf{r}_A(1))\rangle\langle\delta(\mathbf{r}_B(2))\rangle$. The latter quantities are only different from zero if allowance is made for electron correlation in the wave function. The energy $\langle r_{12}^{-1}\rangle$ is, on the other hand, *relatively* little affected by rather strenuous efforts at introducing electron correlation, variations of the order of 10% being typical.

Variation in $\langle z_c(1)z_c(2)\rangle$ is much more drastic. Something more than merely an effective nuclear charge is needed in the wave function and the more complex wave functions do show better values for the end to end correlation. Full discussion of $\langle z_c(1)z_c(2)\rangle$ and also $\langle x_c(1)x_c(2)\rangle$ should be postponed until they have been obtained for the Newell and James-Coolidge functions.

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[17] R. P. Feynman, Phys. Rev. 56, 340 (1939).

[18] Another desirable physical requirement, the virial theorem $\langle V\rangle=-2\langle T\rangle$, is automatically satisfied by incorporating an effective nuclear charge in the trial wave function.

The quantity

$$\frac{\langle\delta(\mathbf{r}_A(1))\delta(\mathbf{r}_B(2))\rangle}{\langle\delta(\mathbf{r}_A(1))\rangle\langle\delta(\mathbf{r}_B(2))\rangle}-1,$$

called the "nuclear correlation," is suggested by the spin-spin coupling constant and proves to have interesting variations. In general, the valence bond functions greatly overemphasize the nuclear correlation; the James-Coolidge function shows that there is relatively little of such correlation in the actual molecule. The nuclear correlation is of interest also because it could be easily imposed as an auxiliary condition which a new trial wave function would have to satisfy as well as minimizing the energy.

In conclusion, the electron correlation built into a wave function affects the expectation values of some two-electron operators much more than others.[19] In particular, the molecular energy is much less sensitive than an operator suggestive of the spin-spin coupling constant.

III. APPLICATIONS TO SPECIFIC POLARIZABILITIES

In the second part of this paper, expectation values of certain functions of the coordinates were listed together with experimental or accurate theoretical results. In this way, the various ground-state wave functions, Ψ_0, are compared. In this third section, the polarizabilities are determined as expectation values of various functions of the coordinates. Comparison of the theoretical polarizabilities with the experimental results raises the following question. Are the errors in the polarizability a result of the errors in Ψ_0 or in the assumed form of the first-order variation functions? These two sources of error can sometimes be separated if the variational procedure leads to expectation values which are known from experiment.

All of the polarizability tensors have been calculated by a variation method and indeed more accurately by Ishiguro[20–22] and co-workers. Our point of view is a little different from theirs. Our interest is to see how far one can go with a very simple variation function, Ψ_1, proportional to Ψ_0 and to compare the results for a number of the well-known wave functions.

A. Electrical Polarizability

In the case of an electric field the polarizability tensor $\alpha_{\kappa\lambda}$ is defined by the equation

$$E=E_0-\tfrac{1}{2}\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\alpha_{\kappa\lambda}\mathcal{E}_\kappa\mathcal{E}_\lambda, \qquad (17)$$

where $\mathcal{E}_\kappa$ and $\mathcal{E}_\lambda$ are components of the electric field. The polarizing Hamiltonian is just

$$\textstyle\sum_k e\mathbf{r}_k\cdot\boldsymbol{\mathcal{E}} \quad \text{or} \quad \mathcal{H}_1(\mathcal{E})=\sum_k e\mathbf{r}_k. \qquad (18)$$

For the perturbation function $\mathbf{P}(\mathcal{E})$ in H_2, we use simply

$$P_\kappa(\mathcal{E})=a_\kappa e r_\kappa(i),$$

where the a_κ are variational parameters and $\mathbf{r}(i)$ is a vector extending from a chosen origin in the molecule to electron i. (For H_2 it is convenient to use the midpoint of the internuclear line as an origin.) The energy of the electron will be

$$E\cong E_0+\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\mathcal{E}_\kappa\mathcal{E}_\lambda\Big\{a_\kappa e^2\langle\Psi_0|r_\kappa r_\lambda|\Psi_0\rangle + a_\lambda e^2\langle\Psi_0|r_\lambda r_\kappa|\Psi_0\rangle + a_\kappa a_\lambda\frac{\hbar^2}{2}\frac{e^2}{m}\langle\psi_0|\delta_{\kappa\lambda}|\Psi_0\rangle\Big\}. \qquad (19)$$

Throughout this paper, the symbol $\cong$ will mean that the equation is true only for a specific choice of variational function. Letting $\partial E/\partial a_\lambda\equiv 0$, one finds

$$a_\lambda=-\frac{2m}{\hbar^2}a_0^2\langle r_\lambda^2\rangle, \qquad (20)$$

where $\langle\ \rangle$ means the dimensionless expectation value of a coordinate operator of a single electron over the ground-state wave function expressed in units of the Bohr radius, a_0. Substituting the value of a_λ back into Eq. (18) for the energy, one has

$$E=E_0-\tfrac{1}{2}\sum_{\kappa=0}^{3}\sum_{\lambda=1}^{3}\mathcal{E}_\kappa\mathcal{E}_\lambda(4a_0^3) \times\{\langle r_\kappa r_\lambda\rangle(\langle r_\kappa^2\rangle+\langle r_\lambda^2\rangle)-\langle r_\kappa^2\rangle\langle r_\lambda^2\rangle\delta_{\kappa\lambda}\}. \qquad (21)$$

For a molecule in a Σ state, the coefficients of the $\mathcal{E}_\kappa\mathcal{E}_\lambda$ vanish for $\kappa\neq\lambda$ so that on comparison of Eqs. (17) and (21), one has

$$\begin{aligned}\tilde{\alpha}_{xx}=\tilde{\alpha}_{yy}=\tilde{\alpha}_\perp&\cong 4a_0^3(\langle x_c^2\rangle)^2,\\ \tilde{\alpha}_{zz}=\tilde{\alpha}_{\parallel}&\cong 4a_0^3(\langle z_c^2\rangle)^2,\end{aligned} \qquad (22)$$

c referring to the origin from which x, y, and z are measured. $\tilde{\alpha}$ is the polarizability tensor per electron. The total polarizability tensor has components twice these values plus a correction for the correlation of the two electrons:

$$\begin{aligned}\alpha_\perp&\cong 8a_0^3\{\langle x_c^2\rangle+\langle x_c(1)x_c(2)\rangle\}^2,\\ \alpha_{\parallel}&\cong 8a_0^3\{\langle z_c^2\rangle+\langle z_c(1)z_c(2)\rangle\}^2.\end{aligned} \qquad (23)$$

Just these equations were derived long ago by Hirschfelder.[23] They are rederived here as part of the

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[19] Barnett, Birss, and Coulson, J. Molecular Phys. **1**, 44 (1958), have recently treated the two-electron operator problem from a slightly different point of view.

[20] E. Ishiguro and S. Koide, Phys. Rev. **94**, 350 (1954).

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

[22] E. Ishiguro, Phys. Rev. **111**, 203 (1958).

[23] J. O. Hirschfelder, J. Chem. Phys. **3**, 555 (1935).

TABLE IV. External field polarizabilities of H_2 ($R=1.4a_0$).

Wave function	Electric dipole polarizability in units of a_0^3		Diamagnetic susceptibility in units of $\alpha^2 a_0^3$			
	$\alpha_\perp$	$\alpha_{\parallel}$	$-\chi_\perp{}^d$	$-\chi_{\parallel}{}^d$	$\chi_\perp{}^p$	$-\chi$
Heitler-London	9.02	12.62	1.211	1.037	0.0978	1.088
Wang	4.72	5.12	0.949	0.767	0.0703	0.841
Weinbaum	4.36	6.18	0.910	0.738	0.0650	0.848
Rosen	4.40	5.04	0.853	0.742	0.0290	0.797
Hirschfelder-Linnett	3.95	5.71	0.907	0.744	0.0585	0.814
Coulson (unshielded)	9.77	16.57	1.206	1.044	0.0438	1.123
Coulson (shielded)	4.35	9.15	0.908	0.742	0.0608	0.841
Wallis (C.I.)	5.32	5.01	0.982	0.816	0.0558	0.889
Wallis (limited ionic)	4.64	6.39	0.935	0.761	0.0645	0.834
Nordsieck			0.877	0.745	0.0200 0.0224	0.820 0.818
Newell			0.867	0.731	0.0210 0.0238	0.808 0.806
Ramsey (exp.)					0.0267	
Ishiguro *et al.* (same as exp.)	4.443	6.107				
Wills and Hector[a] (exp.)						0.829

[a] A. P. Wills and L. G. Hector, Phys. Rev. **23**, 209 (1924).

general program of the computation of polarizability tensors; Table IV compares the molecular polarizabilities produced by this equation when applied to various wave functions. The polarizability values of Ishiguro, Arai, Mizushima, and Kotani were obtained by a variation method starting from the eleven-term James-Coolidge function and are in complete agreement with experiment. One can, however, obtain polarizabilities good to within 5% using very simple wave functions.

The most striking improvement in polarizability comes from the use of an effective $Z>1$ in the exponent of the atomic wave functions. The charge distribution is compressed longitudinally and laterally so that both $\alpha_\perp$ and $\alpha_{\parallel}$ are sharply reduced. At this stage $\alpha_\perp$ is accurate but $\alpha_{\parallel}$ is off owing to the electron correlation term $\langle z_c(1)z_c(2)\rangle$. In general, the simple molecular orbital (MO) treatments ignore this negative term and give too high a value for $\alpha_{\parallel}$ and the simple valence bond (VB) treatments exaggerate it so that $\alpha_{\parallel}$ is too small. Improvement of the VB function by adding ionic terms and of the MO function by adding configuration interaction and ionic character gives excellent results.

The Rosen function in which the charge distribution is longitudinally compressed by $s-p$ hybridization gives too small a value of $\alpha_{\parallel}$. Although they yield about the same dissociation energy (4.0 ev), the charge density of the Weinbaum function is distinctly better than that of the Rosen function.

B. Diamagnetic Susceptibility

In the case of a magnetic field, the susceptibility tensor $\chi_{\kappa\lambda}$ is defined by the equation

$$E=E_0-\tfrac{1}{2}\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}\chi_{\kappa\lambda}H_\kappa H_\lambda, \tag{24}$$

where H_κ and H_λ are components of the magnetic field. The Hamiltonian consists of two parts, a static Hamiltonian and a polarizing Hamiltonian:

$$\frac{1}{8}\frac{e^2}{mc^2}\sum_{\kappa,\lambda}\sum_{k}\left[r_k{}^2\delta_{\kappa\lambda}-r_\lambda(k)r_\kappa(k)\right]H_\kappa H_\lambda+\frac{e}{2mc}\sum_k \mathbf{l}_k\cdot\mathbf{H}. \tag{25}$$

The first term comes from the square of the external vector potential

$$\mathbf{A}_{\mathrm{ext}}(\mathbf{r}_k)=\tfrac{1}{2}\mathbf{H}\times\mathbf{r}_k, \tag{26}$$

and the second term from the cross products between the moments and the external vector potential.[24] A change in gauge will shift the relative weights of the two terms in (25) but not their sum.

Comparing (25) and (24), we obtain the static molecular susceptibilities:

$$\begin{aligned}\chi_{xx}{}^d&=\chi_{yy}{}^d=\chi_\perp{}^d=-\tfrac{1}{2}\alpha^2a_0{}^3\langle y_c{}^2+z_c{}^2\rangle,\\ \chi_{zz}{}^d&=\chi_{\parallel}{}^d=-\tfrac{1}{2}\alpha^2a_0{}^3\langle x_c{}^2+y_c{}^2\rangle.\end{aligned} \tag{27}$$

The perturbation function $\mathbf{P}(H)$ for H_2 is chosen to be

$$\begin{aligned}&P_x(H)=aiy_cz_c,\quad P_z=0,\\ &P_y(H)=aix_cz_c,\end{aligned} \tag{28}$$

where a is a variation parameter. The form of $P(H)$ is explained as follows. The magnetic field induces a magnetic dipole in the molecule which is equivalent to a current so that the real Ψ_0 must be perturbed by a complex part which must transform like an axial vector. On the other hand, if the magnetic field is parallel to the internuclear axis, it cannot perturb the molecule because the polarizing Hamiltonian then commutes with $\mathcal{H}_0$.

From Eq. (13), one finds that the polarization energy

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[24] The origin of r and r_κ is the center of the molecule.

per electron is

$$E-E_0=\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}H_\kappa H_\lambda\left\{\frac{e}{2mc}\langle\Psi_0|l_\kappa P_\lambda(H)+P_\kappa^*(H)l_\lambda|\Psi_0\rangle\right.$$
$$\left.+\frac{\hbar^2}{2m}\langle\Psi_0|\nabla P_\kappa^*(H)\cdot\nabla P_\lambda(H)|\Psi_0\rangle\right\}. \quad (29)$$

Inserting the components of P, one sees that the only nonvanishing coefficients of $H_\kappa H_\lambda$ are those for $\kappa=\lambda=x$ and $\kappa=\lambda=y$ which are equal. Again setting $\partial E/\partial a$ equal to zero and solving for a, one has from Eq. (11)

$$a=\tfrac{1}{2}(\alpha/e)\langle z_c^2-x_c^2\rangle/\langle z_c^2+x_c^2\rangle, \quad (30)$$

$$\tilde{\chi}_{xx}{}^p=\tilde{\chi}_{yy}{}^p\cong\tfrac{1}{2}\alpha^2a_0^3\langle z_c^2-x_c^2\rangle^2/\langle z_c^2+x_c^2\rangle, \quad (31)$$

$\tilde{\chi}$ being the susceptibility per electron.

Again, we observe that the total susceptibility is given by twice the susceptibility per electron plus a correction for electron correlation. The latter correction vanishes in this particular case so that we have

$$\chi_{xx}{}^p=\chi_{yy}{}^p=\chi_\perp{}^p\cong\alpha^2a_0^3\langle z_c^2-x_c^2\rangle^2/\langle z_c^2+x_c^2\rangle. \quad (32)$$

The form of (32) has the following physical explanation. If Larmor's theorem were valid, all the electrons would be rotating about H with an angular velocity $\omega=eH/2mc$. The extra kinetic energy of rotation would then be directly identified with the diamagnetic energy. When the forces acting on the electrons are not central, i.e., when there is more than one nucleus, some of the charge will not rotate about the field, but will remain attached to the nuclei. There will then be a reduction of the total kinetic energy and hence, a reduction in the total diamagnetic susceptibility, i.e., a paramagnetic part. The latter only exists in virtue of the torques exerted on the electron by the nuclei. If the distribution of electrons were spherical, i.e., if $\langle z_c^2-x_c^2\rangle=0$, then the electrons could rotate independently of the nuclei. For the H_2 molecule, there is a great deal of slippage, i.e., the electrons contribute only a small fraction of their share to the moment of inertia of the rotating molecule. This quasi-decoupling of the nuclear and electronic motion is only possible because the electron distribution is not far from spherical.

Equation (32) for the paramagnetic part of the susceptibility was first derived by Tillieu and Guy,[25] and is included here for completeness. Although variation calculations of electrical polarizabilities were numerous in the years 1930–1935, it was not until 1954 that the variation method was applied to magnetic polarization. Unaware of the work of Tillieu and Guy, Espe[26] at the suggestion of A. Bohr applied the identical variation method to determine the moment of inertia of the electrons in a rotating H_2 molecule. In view of Larmor's theorem, this moment of inertia is simply related to the paramagnetic part of the diamagnetic susceptibility.

Table IV contains the calculated diamagnetic susceptibilities. The paramagnetic part contributed only about 3% of the total mean susceptibility but this may well be a special feature of molecules with nearly spherical charge distributions. The static part of the susceptibility which depends on sums like $\langle z_c^2+x_c^2\rangle$ is obtained within an error of 5% or so by most of the wave functions. The paramagnetic part of the susceptibility is quadratic in the difference $\langle z_c^2-x_c^2\rangle$, which is sensitive to the choice of Ψ_0. The calculated values for χ^p illustrate the point that the calculated χ can be either larger or smaller than the true χ. Two values of the paramagnetic susceptibility are quoted for the Nordsieck and Newell functions. The first is for a one-term variational function of the form of Eq. (28); the second is for a four-term variational function,

$$P_x(H)=izy\{c_1+c_2y^2+c_3z^2+c_4y^4\}.$$

Espe has shown that the convergence of the variational procedure is fair; the difference between the one-term and four-term result is about ten percent. This is a little disappointing in view of future applications. However, variations in the small paramagnetic term have a negligible effect on the general good agreement of the theoretical and observed mean susceptibility.

C. Nuclear Magnetic Shielding

The nuclear magnetic shielding is a measure of the magnetic polarizability of a molecule. When a molecule is exposed to a magnetic field, currents proportional to the external field are induced; these currents are measured by measuring their energy of interaction with a magnetic field. This can be the same external field in which case we are measuring the diamagnetic energy $-\frac{1}{2}\mathbf{H}\cdot\chi\mathbf{H}$, or it can be one of the nuclear dipole fields within the molecule in which case we are measuring the energy of magnetic shielding of nucleus N, $-\boldsymbol{\mu}^{(N)}\cdot\sigma\mathbf{H}$. For quantum mechanical purposes, we need the same function $P(H)$ and in measuring the paramagnetic parts of χ or σ, we are merely measuring different expectation values involving P.

The nuclear magnetic shielding tensor at nucleus N, $\sigma_{\kappa\lambda}{}^{(N)}$, is defined by the equation

$$E=E_0-\sum_{\kappa=1}^{3}\sum_{\lambda=1}^{3}(\delta_{\kappa\lambda}-T_{\kappa\lambda}{}^{(N)})\mu_\kappa{}^{(N)}H_\lambda, \quad (33)$$

where $\mu_\kappa{}^{(N)}$ is a component of the magnetic moment vector of nucleus N. The Hamiltonian for the nucleus N again consists of two parts, a static Hamiltonian and a polarizing Hamiltonian:

$$\frac{1}{2}\frac{e^2}{mc^2}\sum_{\kappa,\lambda}\sum_k\frac{[r_k{}^2\delta_{\kappa\lambda}-r_\lambda(k)r_\kappa(k)]}{r_k{}^3}\mu_\kappa{}^{(N)}H_\lambda$$
$$+\frac{e}{2mc}\sum_k\mathbf{l}_k\cdot\frac{2\boldsymbol{\mu}^{(N)}}{r_k{}^3}, \quad (34)$$

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[25] J. Tillieu and G. Guy, Compt. rend. **239**, 1203 (1954); **240**, 1402 (1955).

[26] I. Espe, Phys. Rev. **103**, 1254 (1956).

where the superscript N may now be dropped. The first term comes from the cross products of the nuclear dipole and the external vector potentials; the second term comes from the cross products between the moments and the nuclear dipole vector potentials. A change in gauge will again shift the relative weight of the two terms but not their sum.

We are interested in the simultaneous polarization of the molecule by the terms

$$\frac{e}{2mc}\sum_k \mathbf{l}_k\cdot\mathbf{H} \quad\text{and}\quad \frac{e}{2mc}\sum_k\sum_N \mathbf{l}_k\cdot\frac{\boldsymbol{\mu}^{(N)}}{r_k^3}. \tag{35}$$

A minor difficulty arises because the angular momentum operators $\mathbf{l}_k$ in the two terms are not defined with respect to the same origin in general. In the first term, the angular momenta are defined about the center of the molecule because Eq. (26), i.e., $\mathbf{A}=\frac{1}{2}\mathbf{H}\times\mathbf{r}_c(k)$, has been used for the vector potential. On the other hand, the angular momenta in the nuclear term are most naturally defined with the given nucleus as origin.

In calculating the diamagnetic susceptibility of H_2, the natural origin is the center of the molecule. With respect to that origin, we have determined the wave function of the molecule to first order in the magnetic field, *viz.*:

$$\Psi=[1+\mathbf{H}\cdot\mathbf{P}(H)]\Psi_0. \tag{36}$$

Suppose that we wish to change the origin of the external vector potential and hence the origin of the angular momenta in Eq. (35a). It is *not* necessary to repeat the variation calculation because the change of origin corresponds only to a change in gauge of the vector potential, i.e.,

$$\begin{aligned}\mathbf{A}'&=\tfrac{1}{2}\mathbf{H}\times(\mathbf{r}_c+\mathbf{R})=\mathbf{A}+\nabla\Lambda,\\ \nabla\times\mathbf{A}'&=\nabla\times\mathbf{A}=\mathbf{H},\end{aligned} \tag{37}$$

where $\mathbf{R}$ is an arbitrary constant vector and $\Lambda=\frac{1}{2}\mathbf{r}\cdot\mathbf{H}\times\mathbf{R}$.

Now because a gauge transformation obviously alters the Hamiltonian, the wave function itself must transform in order to leave the Schrödinger equation covariant.[27] The wave function defined with respect to an origin at $\mathbf{R}$ with respect to the center of the molecule[28] is

$$\begin{aligned}\Psi'&=\Psi\exp[(-ie/\hbar c)\Lambda]\\ &=\Psi\exp[(-ie/2\hbar c)\mathbf{r}\cdot\mathbf{H}\times\mathbf{R}].\end{aligned} \tag{38}$$

Inserting Eq. (36) for the wave function Ψ defined with respect to the old gauge, we have

$$\Psi'=\{1+\mathbf{H}\cdot[\mathbf{P}(H)-(ie/2\hbar c)\mathbf{R}\times\mathbf{r}]\}\Psi, \tag{39}$$

where only terms linear in $\mathbf{H}$ have been retained. To calculate the chemical shift it is obviously convenient to use an origin at one of the nuclei so that effectively $\mathbf{P}(H)$ becomes

$$\mathbf{P}'(H)=\mathbf{P}(H)\mp(ieR/4\hbar c)(x\mathbf{j}-y\mathbf{i}). \tag{40}$$

TABLE V. Nuclear magnetic shielding constants[a] for various wave functions of H_2 ($R=1.4a_0$).

Function	$\sigma_\perp{}^d$	$\sigma_{\parallel}{}^d$	$\sigma_\perp{}^p$		σ
Heitler-London	3.03	2.45	−0.59	0.0021	2.44
Wang	2.73	3.40	−0.75	0.0157	2.46
Weinbaum	2.77	3.46	−0.80	0.0117	2.47
Rosen	2.82	3.46	−0.91	0.0350	2.45
Hirschfelder-Linnett	2.85	3.51	−0.84	0.0325	2.53
Coulson (unshielded)	2.47	3.01	−0.57	0.0030	2.27
Coulson (shielded)	2.85	3.54	−0.82	0.0251	2.55
Wallis (C.I.)	2.81	3.49	−0.78	0.0162	2.53
Wallis (limited ionic)	2.68	3.55	−0.98	0.0214	2.33
Exp.			−0.95	···	2.62

$$\sigma=\tfrac{1}{3}(2\sigma_\perp{}^d+2\sigma_\perp{}^p+\sigma_{\parallel}{}^d)$$

[a] All shielding constants have been multiplied by 10^5.

The paramagnetic part of the nuclear magnetic shielding tensor $\sigma_{\kappa\lambda}{}^p$ can now be extracted at once by comparing Eqs. (16) and (33):

$$\sigma_{\kappa\lambda}{}^p=\left\langle\Psi_0\left|\frac{e}{mc}\sum_k\frac{1}{r_k^3}[l_\kappa(k)P_\lambda(H)+P_\lambda{}^*(H)l_\kappa(k)]\right|\Psi_0\right\rangle. \tag{41}$$

For H_2, only the terms $\kappa=\lambda=x$ or y are nonvanishing so that we have

$$\sigma_{xx}{}^p=\sigma_{yy}{}^p=\frac{e}{mc}\left\langle l_x\frac{P_x{}'(H)}{r_H{}^3}\right\rangle\cong-\frac{e\hbar}{mc}a\left\langle\frac{z^2-x^2}{r^3}\right\rangle. \tag{42}$$

Multiplying by two to obtain the final results[29] for the molecule, we have

$$\sigma_\perp{}^d=\alpha^2\left\langle\frac{z^2+x^2}{r^3}\right\rangle,\quad \sigma_{\parallel}{}^d=\alpha^2\left\langle\frac{x^2+y^2}{r^3}\right\rangle, \tag{43}$$

$$\begin{aligned}\sigma_\perp{}^p\cong-\alpha^2\Bigg[&\frac{R}{2}\left\langle\frac{z}{r^3}\right\rangle\\ &+\left\{\left\langle\frac{z^2-x^2}{r^3}\right\rangle-\frac{R}{2}\left\langle\frac{z}{r^3}\right\rangle\right\}\frac{\langle z^2-x^2\rangle}{\langle z^2+x^2\rangle}\Bigg].\end{aligned} \tag{44}$$

Table V presents the chemical shift calculated from Eq. (43) for various wave functions. One is at first surprised by the fact that the experimental value of the paramagnetic part of the shielding σ^p is about one-third of the total mean σ. In contrast, the "high-frequency" or paramagnetic part, χ^p, of the diamagnetic susceptibility is only about 3% of the total mean χ. The explanation is that very little of the experimental σ^p is really of high-frequency origin. In calculating σ^d we used as an ex-

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[27] W. Pauli, *Die Allgemeinem Prinzipien der Wellenmechanik* (Edwards Brothers, Inc., Ann Arbor, 1947), p. 111.

[28] $\mathbf{R}$ will be $\pm\frac{1}{2}R\mathbf{k}$ for the two nuclei of H_2.

[29] These results were first given in T. P. Das and R. Bersohn, Phys. Rev. **104**, 849 (1956). The reader will note that between $1/r$ and what follows the printer omitted a plus sign. The term $1/r$ should have been replaced by $(x^2+z^2)/r^3$.

ternal vector potential $\frac{1}{2}\mathbf{H}\times\mathbf{r}$. To be consistent, in calculating σ^p, we had to do the same thing which introduced the large correction term, $-\alpha^2(R/2)\langle z/r^3\rangle$. If in computing σ^d we had used the vector potential $\frac{1}{2}\mathbf{H}\times\mathbf{r}_c$, the results would have been

$$\sigma_{\perp}{}^{*d}=\alpha^2\left\langle\frac{z(z-\frac{1}{2}R)+x^2}{r^3}\right\rangle,\quad \sigma_{11}{}^{*d}=\alpha^2\left\langle\frac{x^2+y^2}{r^3}\right\rangle,\tag{45}$$

and no correction term would appear in σ^p.

The correction term itself can be evaluated using the principle that the average electric field acting on the electron is zero. That is,

$$-\tfrac{1}{2}\alpha^2R\langle z/r^3\rangle=-\alpha^2/4R=-0.951\times10^{-5},\tag{46}$$

which is almost within experimental error of the observed σ^p. We therefore infer that the remaining terms in Eq. (44) will be negligibly small. The fourth column of figures in Table V shows that these terms are highly variable between the different wave functions but always very small. Ramsey[30] anticipates that the quantity $\langle(z^2-x^2)/r^3\rangle$ may become available and at that time these terms may be separately confronted with experiment.

D. Spin-Spin Interaction

1. Choice of the Fermi Hyperfine Interaction as the Perturbing Hamiltonian

The nuclear spins of a molecule can interact either directly, by a one-electron mechanism, or by a two-electron mechanism.[31] The direct mechanism is the dipole-dipole interaction between the two nuclei:

$$\frac{\boldsymbol{\mu}_A\cdot\boldsymbol{\mu}_B}{R_{AB}{}^3}-\frac{3(\boldsymbol{\mu}_A\cdot\mathbf{R}_{AB})(\boldsymbol{\mu}_B\cdot\mathbf{R}_{AB})}{R_{AB}{}^5}.\tag{47}$$

This interaction, while inherently of order α^{-2} compared to the electron-coupled terms, effectively vanishes in the liquid state because of the random and rapid molecular reorientations.

The one-electron mechanism results from the cross products of the nuclear dipole vector potentials:

$$\frac{e^2}{2mc^2}\mathbf{A}^{(A)}(r_A(k))\cdot\mathbf{A}^{(B)}(r_B(k))\tag{48a}$$

and the simultaneous action of the polarizing terms

$$(e/mc)\mathbf{p}_k\cdot\mathbf{A}^{(A)}(r_A(k))$$

and (48b)

$$(e/mc)\mathbf{p}_k\cdot\mathbf{A}^{(B)}(r_B(k)).$$

Term (48a) involves expectation values of the form $\langle\mathbf{r}_A(k)\cdot\mathbf{r}_B(k)r_A{}^{-3}(k)r_B{}^{-3}(k)\rangle$. Such terms are inherently small because they come from the region of overlap of the wave functions centered on atoms A and B. Moreover, in H_2, the scalar product will change sign in the rather appreciable region of overlap. For HD, Stephen[32] has shown that this term is ~2 cycles. The polarizing terms, (48b), are also inherently small. They involve products of off-diagonal matrix elements of the orbital angular momentum operator and the wave function of H_2 is predominantly of s character. They are small for the same reason that the paramagnetic part of the chemical shift is so small.

The two-electron mechanism results from the simultaneous action of two hyperfine interaction energies,

$$g\beta\mathbf{S}_j\cdot\nabla\times\left(\frac{\boldsymbol{\mu}_A\times\mathbf{r}_A(j)}{r_A{}^3(j)}\right)$$

and

$$g\beta\mathbf{S}_j\cdot\nabla\times\left(\frac{\boldsymbol{\mu}_B\times\mathbf{r}_B(k)}{r_A{}^3(k)}\right).$$

Ramsey[31] has also shown that a two-electron mechanism analogous to (48b) can produce a spin-spin coupling but this is inherently small for the reasons stated above. Stephen showed that the total of all such terms was 0.6–0.7 cycle.

The hyperfine interaction of nucleus A and electron j can be written as the sum of two terms,

$$(16/3)\pi\beta\hbar\gamma_A\mathbf{I}_A\cdot\mathbf{S}_j\delta(\mathbf{r}_A(j)),\tag{49}$$

and

$$2\beta\hbar\gamma_A\{3[\mathbf{S}_j\cdot\mathbf{r}_A(j)][\mathbf{I}_A\cdot\mathbf{r}_A(j)]r_A{}^{-5}(j)-\mathbf{S}_j\cdot\mathbf{I}_Ar_A{}^{-3}(j)\}.\tag{50}$$

A considerable simplification will result if we can drop the angle-dependent terms leaving only the δ-function interaction. The justification for this omission is as follows. There are three types of cross products between the two hyperfine interaction terms—those involving cross products of two δ-function terms, those involving cross products of a δ-function term and an angle-dependent term, and those involving cross products of two angle-dependent terms. In Appendix A it is shown that the cross-terms of the second type are negligible so we are justified in dropping the third type of term.

The preceding paragraphs have been preliminary to the main task which is to obtain the spin-spin coupling constant from products of the δ-function hyperfine interaction. The δ-function interaction contributes very nearly all of the spin-spin coupling constant because it is effective where the electronic wave functions are largest and because it does not contain an angular factor which could vary in sign.

2. Methods of Calculating the Spin-Spin Coupling Constant

The spin-spin coupling constant is the coefficient (when averaged over all orientations of the molecule) of

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[30] See reference 2, p. 166.

[31] N. F. Ramsey, Phys. Rev. **91**, 303 (1953).

[32] M. J. Stephen, Proc. Roy. Soc. (London) **243**, 274 (1957).

$\mathbf{I}_A \cdot \mathbf{I}_B$ in the electronic energy. If the nuclei A, B are in chemically inequivalent positions, this part of the energy can be calculated in three different ways. One method, used by Stephen, is to minimize directly the spin-spin coupling energy which is of order $\gamma_A\gamma_B$. This requires that one determine the perturbation of the ground-state wave function by the magnetic moments of both nucleus A and of nucleus B.

The method which we have used is to minimize the part of the electronic energy proportional to γ_A^2 in order to determine the wave function of the molecule to first order in the magnetic moment of nucleus A. The spin-spin coupling energy is then determined by computing the hyperfine structure of nucleus B in the state of the molecule perturbed by nucleus A. A method, equivalent in principle, involves the determination of the wave function to first order in γ_B. The part of the electronic energy which depends on the nuclear moments can be written as

$$J_{AA}\gamma_A^2+J_{AB}\gamma_A\gamma_B+J_{BB}\gamma_B^2, \tag{51}$$

and the three methods described correspond to minimizing separately each of the three terms. These procedures would be equivalent if the true Ψ_0 had been used to begin the calculation; if not, one has no criterion for preference. It will be interesting, for example, in the molecule HF to compare the values for the spin-spin coupling constants obtained by the three different methods.

Our method differs from Stephen also in the form of the variation function used. In general, one writes for the perturbation produced by the term[33]

$$\begin{gathered}(8\pi/3)g_{\mathrm{el}}\beta\hbar\gamma_A I_{Az}s_{1z}\delta(\mathbf{r}_A(1)),\\ \Psi_1=\lambda_A[s_{1z}f_A(1)+s_{2z}f_A(2)]\Psi_0,\end{gathered} \tag{52}$$

where

$$\lambda_A=(8\pi/3)g_{\mathrm{el}}\beta\hbar\gamma_A I_{Az}/e^2a_0^2.$$

For $f_A(1)$ Stephen used the function

$$sr_A^2(1)+t\delta(\mathbf{r}_A(1)), \tag{53}$$

whereas we use

$$f_A(\lambda_1,\mu_1)=\sum_{p\geq 1}\sum_{q\geq 0} C_{pq}\lambda_1^p\mu_1^q, \tag{54}$$

where $\lambda_1=[r_A(1)+r_B(1)]/R$, $\mu_1=[r_B(1)-r_A(1)]/R$. Numerical results show that the latter function will ultimately fail to be quadratically integrable; this failure is obvious for the former function. The self-coupling constants J_{AA}, J_{BB} are infinite when evaluated with function (53) and have no evident upper limit with function (54). The desired experimental internuclear coupling, J_{AB}, is perfectly finite and apparently convergent with either function. The divergence of the self-coupling constants is discussed in more detail in Appendix B. In short, the wave function is incorrect only in the neighborhood of nucleus A which does not effect the spin-spin coupling constant.

Function (54) exhibits the division of the perturbed state into two states of symmetry ${}^3\Sigma_u$ and ${}^3\Sigma_g$ (odd and even q, respectively). This division, also emphasized by Ishiguro,[22] results from the fact that the interaction of the electron and nucleus has neither even nor odd symmetry with respect to the center of the molecule.

3. *General Expression for the Spin-Spin Coupling Constant*

The perturbing Hamiltonian can be written as

$$\mathcal{H}_{Aj}=(8\pi/3)g_{\mathrm{el}}\beta\hbar\gamma_A a_0^{-3}\mathbf{I}_A\cdot\mathbf{S}_j\delta(\mathbf{r}_A(j)), \tag{55}$$

where the δ-function and angular momentum vectors are expressed in units of a_0^3 and $\hbar$, respectively. If we consider only the z component of the scalar product and let $\lambda_A=(8\pi/3)g_{\mathrm{el}}\beta\hbar\gamma_A/e^2a_0^2$, we have, for the energy of self-coupling of atom A,

$$E_{AA}=2\langle\Psi_0|\mathcal{H}_{A1}+\mathcal{H}_{A2}|\Psi_A\rangle+\langle\psi_A|\mathcal{H}_0-E_0|\psi_A\rangle, \tag{56}$$

where ψ_A is the molecular wave function perturbed to first order in γ_A.

The expectation values implied by Eq. (56) must now be carried out:

$$\begin{aligned}2\langle\Psi_0|\mathcal{H}_{A1}+\mathcal{H}_{A2}|\Psi_A\rangle&=4\langle\Psi_0|\mathcal{H}_{A1}|\psi_A\rangle\\ &\cong 4\lambda_A^2\langle\Psi_0|\delta(\mathbf{r}_{1A})S_{1z}[S_{1z}f(1)+S_{2z}f(2)]|\Psi_0\rangle,\end{aligned} \tag{57}$$

where Eq. (52) has been substituted for Ψ_A.

Summing over the spins, one has

$$\lambda_A^2\langle\Psi_0|\delta(\mathbf{r}_A(1))[f(1)-f(2)]|\Psi_0\rangle. \tag{58}$$

Now f can always be written as the sum of an even and odd function with respect to inversion in the center of the molecule:

$$f=f_g+f_u,$$

so that the term becomes

$$\begin{aligned}E_{AA}=\lambda_A^2\{&\langle\delta(\mathbf{r}_A(1))[f_g(1)f_u(1)]\rangle\\ &-\langle\delta(\mathbf{r}_A(1))f(2)\rangle\}.\end{aligned} \tag{59}$$

After the energy minimization has been carried out, the term $\langle\Psi_A|\mathcal{H}_{A1}+\mathcal{H}_{A2}|\Psi_0\rangle$ will be the negative of $\langle\Psi_A|\mathcal{H}_0-E_0|\Psi_A\rangle$ so that the self-coupling energy of atom A will be just

$$\begin{aligned}E_{AA}=\tfrac{1}{2}\lambda_A^2\{&\langle\delta(\mathbf{r}_A(1))[f_g(1)+f_u(1)]\rangle\\ &-\langle\delta(\mathbf{r}_A(1))f(2)\rangle\}.\end{aligned} \tag{60}$$

The spin-spin coupling energy between nuclei A and B is

$$\begin{aligned}E_{AB}&=\langle\Psi_0+\Psi_A|\mathcal{H}_{B1}+\mathcal{H}_{B2}|\Psi_0+\Psi_A\rangle\\ &=4\langle\Psi_0|\mathcal{H}_{B1}|\Psi_A\rangle\\ &=4\lambda_A\lambda_B\langle\Psi_0|S_{1z}\delta(\mathbf{r}_{1B})\{S_{1z}f(1)+S_{2z}f(2)\}|\Psi_0\rangle.\end{aligned} \tag{61}$$

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[33] An analogous function can be written for the perturbation produced by the $I_{Ax}S_{1x}$, $I_{Ay}S_{1y}$ terms. In the approximation that the classical dipole-dipole term is omitted, the spin-spin coupling constant will be isotropic so that only one of the terms of the scalar product $\mathbf{I}_A\cdot\mathbf{S}_1$ needs to be considered explicitly.

Summing over the spins, substituting and dropping the explicit Ψ_0, we have

$$\lambda_A\lambda_B\{\langle\delta(\mathbf{r}_B(1))[f_g(1)+f_u(1)]\rangle-\langle\delta(\mathbf{r}_B(1))f(2)\rangle\}. \quad (62)$$

In order to compare the expressions for the self- and mutual coupling constants, we introduce the obvious symmetry relations

$$\begin{aligned}\langle\delta(\mathbf{r}_B(1))f_g(2)\rangle&=\langle\delta(\mathbf{r}_A(1))f_g(2)\rangle,\\ -\langle\delta(\mathbf{r}_B(1))f_u(2)\rangle&=\langle\delta(\mathbf{r}_A(1))f_u(2)\rangle,\end{aligned} \quad (63)$$

which are valid because nuclei A and B are in equivalent positions.

Substituting these relations in E_{AA} and E_{AB}, one obtains[34]

$$\begin{aligned}E_{AA}&=\tfrac{1}{2}\lambda_A{}^2\langle\delta(\mathbf{r}_A(1))[f_g(1)-f_g(2)+f_u(1)-f_u(2)]\rangle,\\ E_{AB}&=\lambda_A\lambda_B\langle\delta(\mathbf{r}_A(1))[f_g(1)-f_g(2)-f_u(1)+f_u(2)]\rangle.\end{aligned} \quad (64)$$

The rather odd result which emerges can be recast as follows:

$$\begin{aligned}E_{AA}&=\tfrac{1}{2}\lambda_A{}^2(J_g+J_u),\\ E_{AB}&=\lambda_A\lambda_B(J_g-J_u).\end{aligned} \quad (65)$$

In actual application the quantities J_g and J_u gradually diverge with increasing number of terms in the wave function. Their difference which is essentially the spin-spin coupling constant is convergent.

4. *Numerical Results*

Calculations were performed only for the single configuration molecular orbital with effective nuclear charge $Z=1.197$ referred to previously as Coulson's effective Z function. For this function

$$\begin{aligned}2\langle\Psi_0|\mathcal{H}_{A1}+\mathcal{H}_{A2}|\Psi_A\rangle&=\lambda_A{}^2|\psi_0(A)|^2\textstyle\sum_p\sum_q c_{pq}[(-)^q-\langle\lambda^p\mu^q\rangle]\\ &=(e^2/a_0)\lambda_A{}^2\textstyle\sum_p\sum_q K_{pq}c_{pq}.\end{aligned} \quad (66)$$

Also

$$\begin{aligned}\langle\Psi_A|\mathcal{H}_0-E_0|\Psi_A\rangle&=\left\langle\Psi_A\middle|T-\frac{T\Psi_0}{\Psi_0}\middle|\Psi_A\right\rangle\\ &=2\left\langle\Psi_A\middle|T_1-\frac{T_1\Psi_0}{\Psi_0}\middle|\Psi_A\right\rangle.\end{aligned} \quad (67)$$

Substituting Eq. (52) for Ψ_A, one has

$$2\frac{\lambda_A{}^2}{4}\left\langle\Psi_0\middle|[f(1)-f(2)]\left[T_1-\frac{T_1\Psi_0}{\Psi_0}\right]\times[f(1)-f(2)]\middle|\Psi_0\right\rangle. \quad (68)$$

Integrating by parts repeatedly, this expression simplifies to

$$\begin{aligned}&\tfrac{1}{2}\lambda_A{}^2(e^2/a_0)\langle|\nabla_1 f(1)|^2\rangle\\ &=\tfrac{1}{2}\lambda_A{}^2(e^2/a_0)\textstyle\sum_p\sum_q\sum_{p'}\sum_{q'}L_{pq,\,p'q'}c_{pq}c_{p'q'}.\end{aligned} \quad (69)$$

The total energy of self-coupling of atom A is

$$E_{AA}=\tfrac{1}{2}\lambda_A{}^2(e^2/a_0)\times\textstyle\sum_p\sum_q\{\sum_{p'}\sum_{q'}L_{pq,\,p'q'}c_{p'q'}+2K_{pq}\}c_{pq}.$$

This energy is then minimized and the resulting simultaneous linear equations are solved for the c_{pq}. The form of $L_{pq,\,p'q'}$ is such that q and q' must be both even or both odd; that is, the equations for c_{pq} with odd q are completely separate from those for even q. The results for the separate parts of the energy are given in Table VI and using (65) the spin-spin coupling constant.

TABLE VI. Spin-spin coupling constant.[a,b]

p,q	J_g	p,q	J_u	E_{AB}/h cps
0,2	−0.09460	0,1	−0.20963	18.75
0,4	−0.12908	0,3	−0.25561	29.67
0,6	−0.12778	0,5	−0.29109	37.99
0,8	−0.12412	0,7	−0.33104	48.13
0,10	−0.11346	0,9	−0.36626	58.80
1,0	−0.21131	1,1	−0.40201	44.36
1,2	−0.25525	1,3	−0.43104	40.89
1,4	−0.28490	1,5	−0.42671	32.98
2,0	−0.30410	2,1	−0.42577	28.30

[a] The experimental value of E_{AB}/h is 42.7 ± 0.7 cps [J. F. Wimett, Phys. Rev. **91**, 476 (1953)].

[b] At each stage of approximation the given p,q was used as well as all those preceding.

The divergence of the self-couplings J_g and J_u, while in principle of no consequence, means that the observable spin-spin coupling constant is obtained as the difference between two divergent quantities. To obtain a convergent result for the spin-spin coupling constant, one must subtract for any p the contributions of adjacent q; any other procedure would lead to arbitrary answers for the spin-spin coupling constant.

Our result oscillates in an unhappy fashion. We do not at present know whether the oscillation is due to numerical error in the calculation or to incorrect treatment of the divergent energies, or is inherent in the variation function. It is encouraging, however, that the result is never too far from the experimental value even though the calculation used a very simple wave function.

IV. CONCLUSIONS

Radio-frequency spectroscopy has introduced new molecular quantities, the electric field gradient at the nucleus, the nuclear magnetic shielding constant, and the spin-spin coupling constant. The aims of this paper have been, using the hydrogen molecule as a model, (1) to show the relation of the new molecular quantities to the older ones which do not depend on the existence of nuclear multipole moments, and (2) to present new methods of calculating these new quantities, especially the polarizations.

The comparison of various expectation values which

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[34] The term "two-electron mechanism" might possibly be misleading here because the final result contains both one-electron and two-electron terms. The spin-spin coupling constant for HD$^+$, for example, would be obtained by deleting the two-electron terms in Eq. (64).

has been made shows from what diverse viewpoints one can approach the hydrogen molecule wave function. When new wave functions are introduced for the hydrogen molecule, it will be very helpful to obtain similar expectation values to exhibit improvements in the wave function. The expectation values have demonstrated that the introduction of an effective nuclear charge is of overriding importance. In addition, the use of $s-p$ hybrid functions with independent effective nuclear charges may prove to be a considerable advance in the valence theory of simple molecules.

In this paper, details have been given of our variation method for calculating chemical shifts. A variation method has been presented for the spin-spin coupling constant but in the course of preparing the manuscript, very similar work by Ishiguro and Stephen has appeared. The variation method appears in general to be rapidly convergent. This is probably because the virtual continuum states are better handled than in the conventional sum over excited states perturbation treatment. Also, the choice of a variation function $\Psi_1=P\Psi_0$, where P contains the variation parameters additively, automatically results, as can be shown, in the satisfaction of the equation

$$\langle\Psi_1|(\mathcal{H}_0-E_0)\Psi_1+(\mathcal{H}_1-E_1)\Psi_0\rangle=0.$$

In principle one wants the right-hand side of the scalar product to vanish identically, but at least a good beginning has been made with this choice of function. Any perturbation method no matter how rapidly convergent gives results no better than the Ψ_0 from which one starts. The variation procedures, because they are rapidly convergent, may help to establish the relative quality of various trial wave functions.

The methods given here can be extended straightforwardly to polyatomic molecules whose observed chemical shifts and spin-spin couplings can then be compared with theoretical calculations. Radio-frequency spectroscopy will then supply us with a deeper insight into the approximate wave functions of more complex molecules as well as of hydrogen.

ACKNOWLEDGMENTS

We are indebted to Dr. M. Barnett for sending his indispensable table of molecular zeta functions. The staff of the Cornell Computing Center performed much of the numerical work. We received helpful suggestions from Professor A. Nordsieck, Professor N. F. Ramsey, Professor A. Abragam, Professor W. Lamb, and Professor C. Coulson. One of us (R. B.) would like to thank Professor A. Kastler and Professor A. Abragam for their cordial hospitality at their Laboratories in France where this paper was finished during a sabbatical leave. The other author (T. P. D.) would like to thank Professor E. L. Hahn for his hospitality at his laboratory in the University of California, Berkeley, where a portion of this work was performed.

APPENDIX A. CROSS PRODUCTS OF THE DIPOLE-DIPOLE AND THE DELTA FUNCTION HYPERFINE TERMS

Consider a hydrogen molecule perturbed by the potential

$$\mathcal{H}_1=-\sum_{k=1}^{2} g\beta\hbar\gamma_A I_{Az}S_{kz}\frac{[3z_A{}^2(k)-r_A{}^2(k)]}{r_A{}^5(k)} \tag{A1}$$

$$=-\sum_{k=1}^{2}\frac{3}{8\pi}\lambda_A\frac{(3\cos^2\theta_k-1)}{r_A{}^3(k)}. \tag{A2}$$

We want to determine by means of the equation

$$(\mathcal{H}_0-E_0)\Psi_1=-\mathcal{H}_1\Psi_0, \tag{A3}$$

the first order modification of the wave function. To this end we can use one of the Ψ_0 determined by the variation method and then apply the variation method again to obtain an approximate function Ψ_1. An alternate procedure is to replace the approximate Ψ_0 by a still cruder approximation and then to integrate Eq. (A3) exactly.

Specifically we assume a single configuration molecular orbital function,

$$\Psi_0(1,2)=\psi_0(1)\psi_0(2),$$

and let

$$\psi_0(1)=[2(1+S)]^{-\frac{1}{2}}[a(1)+b(1)] \tag{A4}$$

$$=[\tfrac{1}{2}(1+S)]^{\frac{1}{2}}a(1)+[2(1+S)]^{\frac{1}{2}}[b(1)-Sa(1)]. \tag{A5}$$

The two terms in Eq. (A5) are orthogonal to each other and the coefficient of $a(1)$ is, using Coulson's $Z=1.193$, equal to $(0.85)^{\frac{1}{2}}$. In other words, 85% of the molecular orbital can be written as a $1s$ function centered an atom A. The second term of (A5) is neglected for the present approximate purpose.

The Hamiltonian (A2) contains the angle θ_k between the vector going to electron k and an arbitrary z axis. By means of the Legendre polynomial addition theorem, one can write

$$(3\cos^2\theta_k-1)=P_2(\theta_A)(3\cos^2\theta_{kA}-1), \tag{A6}$$

where θ_A is the angle between the bond axis and the z axis, the θ_{kA} is the angle between the electron vector and the bond axis.

This equation is not an identity; the terms which are lacking have been dropped because they will not contribute to the final answer. We only wish to obtain, for ψ_1, the d function which is of σ symmetry about the bond axis.

The wave function

$$\psi_0(1)=\left[\frac{(1+S)Z^3}{2\pi}\right]^{\frac{1}{2}}e^{-Zr_{1A}} \tag{A7}$$

is the $1s$ function of a pseudohydrogen atom with an energy

$$E_0=-Z^2e^2/2a_0.$$

When this ψ_0^{ps} and E_0 are substituted in Eq. (A3) one obtains

$$\Psi_1=\left[\frac{(1+S)Z^3}{2\pi}\right]^{\frac{1}{2}}e^{-Zr_A(1)}\left(1+\frac{Zr_A(1)}{3}\right)P_2(\theta_A). \quad \text{(A8)}$$

In the state perturbed to first order by the dipole-dipole interaction of an electron with nucleus A, we must compute the energy of interaction of the same electron with nucleus B. If we let

$$\mathcal{H}_1'=(8\pi/3)g_{\mathrm{el}}\beta\hbar\gamma_B I_{Bz}S_{kz}\delta(\mathbf{r}_B(1))=\lambda_B\delta(\mathbf{r}_B(1)), \quad \text{(A9)}$$

then we desire the term containing $\lambda_A\lambda_B$ in the energy which is

$$4\langle\Psi_1|\mathcal{H}_1'|\Psi_0\rangle=4\Psi_1(r_A=R)\lambda_B\Psi_0(r_B=0). \quad \text{(A10)}$$

Evaluating this expression by means of (A4) and (A8) one obtains for the spin-spin coupling energy

$$\lambda_A\lambda_B\frac{1}{4\pi^2}\frac{Z^3}{R}e^{-ZR}\left(1+\frac{ZR}{3}\right)(1+e^{-ZR})P_2(\theta_A),$$

which is equal to

$$4.0P_2(\theta_A)I_{Az}I_{Bz}\ \text{cps} \quad \text{for} \quad \text{HD}.$$

This particular interaction vanishes for an HD molecule subject to rapid collisions in a liquid or a gas because of the averaging of $P_2(\theta_A)$. However, the magnitude suggests that the dipole-dipole interaction is not important for the spin-spin coupling constant. This is further shown by the almost isotropic J tensor obtained by Stephen. We conjecture that the argument holds generally for spin-spin coupling involving the hydrogen atom and perhaps even still more generally for atoms whose valence electron is mainly s-like.

APPENDIX B. DIVERGENCE OF THE SELF-COUPLING CONSTANT

The divergence of the self-coupling constant J_{AA} and the apparent singularity of the wave function are at first sight disturbing. We must first remark that the δ-function interaction is derived from the same potential energy as the r^{-3} dipole-dipole term. As a formal matter, the r^{-3} term does not permit a stable bound-state solution. The mathematical inference is that the hyperfine interaction term cannot be applied without change to all orders but must be modified. Physically, the trouble comes from the assumption of a point proton magnetic dipole.

Investigations performed on the hydrogen atom itself help clarify the situation. For the present purpose, we are interested in all corrections to the hyperfine structure of magnitude

$$\frac{\langle 0|\mathcal{H}_{\mathrm{hfs}}|n\rangle\langle n|\mathcal{H}_{\mathrm{hfs}}|0\rangle}{E_0-E_n},$$

which means corrections of order $\alpha^2 m/M$ to the hyperfine interaction. These corrections can arise from different sources including (a) recoil effects of the nucleus in its interaction with the electron, (b) finite size of the nucleus which changes the interaction at distances of the order of a meson Compton wavelength, and (c) virtual emission and absorption of a photon by the electron while it is interacting twice with the nuclear moment.

These contributions are presumably beyond the limit of present experimental accuracy in determination of the hydrogen atom hyperfine structure interaction. Contributions of type (a)[35] and (b)[36] have been evaluated only up to terms of order $\alpha m/M$. The proton recoil terms were shown to originate from virtual photons with energy greater than mc^2 and to diverge logarithmically with photon energy. Moreover they depend on the wave function of the hydrogen atom only in the form $|\psi(0)|^2$ so that the considerations would be almost identical for a hydrogen molecule. The third contribution, (c), the electron size effect, is finite but is a correction to the Lamb shift rather than the hyperfine structure because it is proportional[37,38] to I^2S^2.

The divergence of the self-coupling constant for the hydrogen atom is due ultimately to our inadequate knowledge of the charge distribution of the nucleon. A more nearly correct theory will modify the interactions and wave functions only at high momentum, that is, only at distances of the order of 10^{-12} cm from the nucleus; this local modification can hardly change the wave function at distances of the order of 10^{-8} cm, i.e., at the other nucleus. The self-coupling energy of the atom, whether it diverges logarithmically (relativistic treatment) or linearly (nonrelativistic treatment), is in any case to be differentiated from the desired spin-spin coupling energy. The wave function, which is incorrect at very short distances and gives an incorrect, indeed infinite, value for the self-coupling, will nevertheless be correct at large distances and give the correct value for the spin coupling constants.

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[35] R. Arnowitt, Phys. Rev. **92**, 1002 (1953); W. A. Newcomb and E. E. Salpeter, Phys. Rev. **97**, 1146 (1955).

[36] A. C. Zemach, Phys. Rev. **104**, 1771 (1956).

[37] H. M. Fried (private communication).

[38] One might expect a contribution to the spin-spin coupling constant from terms of type (c) in which an electron emits a virtual photon, interacts with the magnetic moment of nucleus A, then with that of B, and then absorbs the virtual photon. Such a process, however, can only make an appreciable contribution when the nuclei are simultaneously within a distance $\hbar/mc$ of the electron.