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# *g* factors and related magnetic properties of molecules. Formulation of theory and calculations for $H_2{}^+$, $HD^+$, and $D_2{}^+$

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A theoretical framework is presented from which precise electronic *g* values for molecules may be calculated. The theory is applied to the calculation of *g* factors and related magnetic properties for $H_2{}^+$, $HD^+$, and $D_2{}^+$. The average *g* value for the ground state of each of these molecular ions is predicted to be shifted by about 3 ppm from the *g* factor for atomic hydrogen. The results are expected to be accurate to about 0.1 ppm, and when compared with future experimental measurements may provide the first precise test of the theory of molecular *g* factors.

## I. INTRODUCTION

The interaction of an atom or a molecule with an external magnetic field provides an important source of information concerning both the nature of the electromagnetic interaction and also the structure and dynamics of the composite atomic or molecular system. In the case of atoms this information is contained primarily in the Landé $g_J$ factor, which determines the magnitude of the interaction between the atom and the external field $\vec{B}$ when this interaction arises from the total electronic angular momentum $\vec{J}$ of the atom:

$$\mathcal{H}^{\text{eff}}_{\text{atom}} = \mu_B g_J \vec{J}\cdot\vec{B} \ , \tag{1}$$

where $\mu_B$ is the Bohr magneton. In the case of molecules the corresponding interaction is described similarly:

$$\mathcal{H}^{\text{eff}}_{\text{molecule}} = \mu_B \vec{S}\cdot\vec{g}\cdot\vec{B} \ , \tag{2}$$

where $\vec{S}$ is the total electron spin,[1] and where the *g* factor is written in tensor form to indicate the interaction may be different for different orientations of the molecule with respect to the magnetic field. In recent times there has been a renewed interest in the precise theory[2-8] and measurement[9-19] of atomic $g_J$ values which has resulted in a detailed understanding of the Zeeman effect for simple atoms. In the case of molecules such understanding has been limited because most experimental work has been restricted to large molecules for which precise quantitative theoretical work is very difficult. Consequently the theoretical calculations have usually been very approximate or have been parametrized to fit the experimental data. In fact there appears to be no precise *ab initio* calculation of the *g* factors for any molecule. An important first step toward a better understanding of molecular *g* factors would be to perform an exact calculation for the simplest paramagnetic molecule, the hydrogen molecular ion, and to compare the results of this calculation with experiment. Preliminary results of this effort have already been reported.[20] Although no precise experimental measurement has yet been made for $H_2{}^+$ or its isomeric relatives, rapidly developing experimental techniques, particularly ion trapping methods, make it seem likely that such measurements will soon be feasible.[21] The information we hope to gain from such studies will differ in important ways from that obtained from similar studies on atoms, since molecules possess vibrational and rotational as well as electronic and translational degrees of freedom, and since such studies may lead to an increased understanding of the nature of the chemical bond and its relation to the Zeeman effect.

Consequently, then, the purpose of this paper is to formulate a theory of *g* factors for molecules and to apply the theory to the particular cases of $H_2{}^+$ and its isotopic relatives. Although the theory of the molecular *g* tensor has been given in a number of places to various degrees of approximation,[22-24] I thought it worthwhile to present here a formulation which, at least in its most general form, accurately includes radiative and nuclear mass corrections as well as the lower-order relativistic corrections to the Hamiltonian describing the Zeeman effect, and thus represents a more complete theoretical formulation of the subject than is usually given.

In Sec. II, I present as a starting point the Breit formalism extended to include radiative and nuclear motion corrections. The initial formulation is formally the same as one I have previously presented for atoms[5] and the development is also quite similar. In the second stage of the formulation a restriction is made to diatomic molecules in preparation for the $H_2{}^+$ calculations, although a simple generalization of the treatment should be possible for polyatomics. A convenient choice of internal coordinates similar to that for the atomic case is made. A unitary transformation of the extended Breit equation is performed which partially separates the center-of-mass coordinate from the internal coordinates. The resulting equation is reduced to nonrelativistic form and the terms which contribute to the $g$ tensor identified and interpreted. At this stage, nuclear mass corrections of order $\alpha^2 m/M$ or higher are ignored and restriction is made to one-electron systems ($H_2^+$). Then, following Pryce,[22] a modified second-order degenerate perturbation theory is used to construct an effective Hamiltonian which operates entirely within the linear manifold associated with the ground electronic state. An explicit expression for the $g$ tensor is obtained from this effective Hamiltonian. It is found that the $g$-tensor expression can be written in a very simple form[20]: a "relativistic mass" term is proportional to the average kinetic energy of the electron, and a second term is proportional to the nuclear magnetic shielding tensor, the theory of which has been given by Ramsey.[25] At this stage the expression for the $g$ tensor is simplified further by neglecting radiative terms of order $\alpha^3$. This gives a final expression for the $g$ tensor which is accurate to order $\alpha^2$.

In Sec. III numerical calculations of the components of the $g$ tensors for $H_2^+$, $HD^+$, and $D_2^+$ are described and the results interpreted. The molecular wave function is obtained in the adiabatic approximation and calculations are performed in a frame of reference which is fixed relative to the internuclear axis. The zero-order (magnetic field absent) part of the electronic wave function is taken from the calculations of Hunter and Pritchard.[26] The first-order (magnetic-field-dependent) part of the electronic wave function is obtained by means of a variation-perturbation scheme. The $g$-tensor components and their contributing terms, i.e., the electron's average kinetic energy and the components of the nuclear magnetic shielding tensor, are calculated as functions of internuclear distance, tabulated and compared with previous calculations. It is found that the average $g$ value for $H_2^+$ at the equilibrium internuclear distance is shifted by about 3 ppm (parts per million) from the $g$ value for atomic hydrogen. This difference is interpreted as primarily due to the increase in the relativistic mass of the electron as the chemical bond is formed between the H atom and the bare proton. Values of the $g$ tensor for some particular vibrational-rotational (VR) states are then calculated. It is found that these values depend on the *average* internuclear distances for the VR states in essentially the same way as the $g$ values vary with the internuclear distance in the adiabatic approximation. Finally, the effective magnetic Hamiltonian containing the components of the $g$ tensor is rewritten in a form convenient for use in the laboratory frame.

In Sec. IV an interesting relationship between the second-order part of the nuclear magnetic shielding tensor and the second-order part of the electron spin-rotation tensor is pointed out. This result leads to a relationship between the spin-rotation tensor and the electronic $g$ tensor. Numerical calculations are performed which examine some consequences of these relationships in the case of $H_2^+$.

Finally, a brief summary of this work is given in Sec. V.

## II. THEORY

A satisfactory starting point for a precise theory of molecular $g$ factors is the extended Breit formalism, which has been developed previously for applications to many-electron atoms.[5] This formalism accurately includes anomalous magnetic moment and nuclear mass correction terms and is expected to give accurate results for the Zeeman effect of a many-electron system to order $\alpha^4 \mu_B B$ where $\alpha = (137.03602)^{-1}$ is the fine-structure constant. According to the theory the stationary states of an atom or molecule in a constant uniform external magnetic field $\vec{B}$ are described by the extended Breit equation

$$\mathcal{H}\Psi(\vec{r}_1, \vec{r}_2, \ldots) = E\Psi(\vec{r}_1, \vec{r}_2, \ldots) \ , \tag{3}$$

where, in natural units ($\hbar = c = 1$),

$$\mathcal{H} = \sum_r \mathcal{H}(r) + \sum_{r<s} U(r,s) \ , \tag{4}$$

$$\mathcal{H}(r) = \vec{\alpha}_r \cdot \vec{\pi}_r + \beta_r m_r - \kappa_r(\beta_r \vec{\sigma}_r \cdot \vec{B}_r - i\beta_r \vec{\alpha}_r \cdot \vec{E}_r) \ , \tag{5}$$

$$\begin{aligned} U(r,s) = e_r e_s r_{rs}^{-1} \left(1 - \frac{\vec{\alpha}_r \cdot \vec{\alpha}_s}{2} - \frac{\vec{\alpha}_r \cdot \vec{r}_{rs} \vec{\alpha}_s \cdot \vec{r}_{rs}}{2r_{rs}^2}\right) \\ + \beta_r \beta_s \kappa_r \kappa_s \left(\frac{\vec{\sigma}_r \cdot \vec{\sigma}_s}{r_{rs}^3} - \frac{3\vec{\sigma}_r \cdot \vec{r}_{rs} \vec{\sigma}_s \cdot \vec{r}_{rs}}{r_{rs}^5} \right. \\ \left. - \tfrac{8}{3}\pi \vec{\sigma}_r \cdot \vec{\sigma}_s \delta^3(\vec{r}_{rs})\right) \ , \end{aligned} \tag{6}$$

$$\vec{\pi}_r = \vec{p}_r - e_r \vec{A}_r \ , \tag{7}$$

$$\vec{A}_r = \tfrac{1}{2}\vec{B} \times \vec{r}_r \ , \tag{8}$$

$$\vec{B}_r = \vec{B} + \sum_{s(\neq r)} e_s \vec{\alpha}_s \times \vec{r}_{rs}/r_{rs}^3 \ , \tag{9}$$

$$\vec{E}_r = \sum_{s(\neq r)} e_s \vec{r}_{rs}/r_{rs}^3 \ . \tag{10}$$

Here $\vec{\pi}_r$ is the mechanical momentum for the $r$th particle, $\vec{A}_r$ is the magnetic vector potential at the coordinate $\vec{r}_r$ in the laboratory frame, $\vec{B}_r$ and $\vec{E}_r$ are the magnetic and electric fields experienced by particle $r$, $\kappa_r$ is the anomalous magnetic moment of particle $r$, and the other symbols have their usual meanings. In Eqs. (3) and (4) and in what follows I use summation indices $i, j, k$ to denote electrons, $X, Y, Z$ to denote nuclei, and $r, s, t$ to denote both electrons and nuclei. At this stage the theory is quite general and is applicable to both atomic and molecular systems.[27] From now on, however, I will restrict the theory to diatomic molecules, which is convenient for the subsequent application to $H_2^+$, although in what follows one could treat polyatomic molecules by a simple generalization. It is now convenient to make a transformation of variables from the set $(\vec{r}_A, \vec{r}_B, \vec{r}_i)$ ($A$ and $B$ will be used to label the two respective nuclei) to the set of center-of-mass and internal coordinates $(\vec{R}_{\text{c.m.}}, \vec{R}_{BA}, \vec{r}_{iC})$ where

$$\vec{R}_{\text{c.m.}} = \sum_r \frac{m_r}{M}\vec{r} = \frac{M_A}{M}\vec{r}_A + \frac{M_B}{M}\vec{r}_B + \sum_i \frac{m}{M}\vec{r}_i \,, \tag{11}$$

$$\vec{R}_{BA} = \vec{r}_B - \vec{r}_A \,, \tag{12}$$

$$\vec{r}_{iC} = \vec{r}_i - \vec{r}_C \,,$$

where

$$\vec{r}_C = (M_A + M_B)^{-1}(M_A\vec{r}_A + M_B\vec{r}_B) \tag{13}$$

and where $M = M_A + M_B + \sum_i m_i$ is the sum of the rest masses of the particles. This choice of internal coordinates reduces to the set used previously for atoms[5] if we let $\vec{r}_B = \vec{r}_A$ and set $M_A = 0$ or $M_B = 0$. The momenta conjugate to $\vec{R}_{\text{c.m.}}$, $\vec{R}_{BA}$ and $\vec{r}_{iC}$ are, respectively,

$$\vec{P}_{\text{c.m.}} = \vec{p}_A + \vec{p}_B + \sum_i \vec{p}_i \,, \tag{14}$$

$$\vec{P}_{BA} = (M_A + M_B)^{-1}(M_A\vec{p}_B - M_B\vec{p}_A) \,, \tag{15}$$

$$\vec{p}_{iC} = \vec{p}_i - \frac{m}{M}\sum_j \vec{p}_j - \frac{m}{M}(\vec{p}_A + \vec{p}_B) \,. \tag{16}$$

The inverse relations are

$$\vec{r}_A = \vec{R}_{\text{c.m.}} - (M_A + M_B)^{-1}M_B\vec{R}_{BA} - \frac{m}{M}\sum_i \vec{r}_{iC} \,, \tag{17}$$

$$\vec{r}_B = \vec{R}_{\text{c.m.}} + (M_A + M_B)^{-1}M_A\vec{R}_{BA} - \frac{m}{M}\sum_i \vec{r}_{iC} \,, \tag{18}$$

$$\vec{r}_i = \vec{R}_{\text{c.m.}} + \vec{r}_{iC} - \frac{m}{M}\sum_j \vec{r}_{jC} \,, \tag{19}$$

$$\vec{p}_A = (M_A/M)\vec{P}_{\text{c.m.}} - \vec{P}_{BA} - (M_A + M_B)^{-1}M_A\sum_i \vec{p}_{iC} \,, \tag{20}$$

$$\vec{p}_B = (M_B/M)\vec{P}_{\text{c.m.}} + \vec{P}_{BA} - (M_A + M_B)^{-1}M_B\sum_i \vec{p}_{iC} \,, \tag{21}$$

$$\vec{p}_i = (m/M)\vec{P}_{\text{c.m.}} + \vec{p}_{iC} \,. \tag{22}$$

Here, as in the atomic case, the quantity

$$\vec{Q} = \sum_r (\vec{p}_r + e_r\vec{A}_r) \tag{23}$$

is a constant of the motion whose vector components commute with each other for an electrically neutral system. Consequently, for a neutral molecule, the exact solution to Eq. (3) can be written in the form

$$\Psi(\vec{R}_{\text{c.m.}}, \vec{R}_{BA}, \vec{r}_{iC}) = \psi(\vec{R}_{BA}, \vec{r}_{iC})e^{i\vec{\pi}\cdot\vec{R}_{\text{c.m.}}} \,, \tag{24}$$

where

$$\vec{\pi} = \vec{K} - \sum_r e_r\vec{A}_r \tag{25}$$

and where $\vec{K}$ is the eigenvalue of the operator $\vec{Q}$. In the case of an electrically charged molecule ion we perform a similar, but only partial, separation of the center-of-mass coordinate by applying a unitary transformation to Eq. (3) with the unitary operator

$$U = \exp\left(-i\sum_r e_r\vec{A}_r\cdot\vec{R}_{\text{c.m.}}\right) . \tag{26}$$

This transformation has been found to describe the motional terms in the Hamiltonian in a particularly transparent way.[3,5,28] The resulting transformed Eq. (3) is found to have exactly the same form as that given in Eqs. (4)–(6), but with the mechanical momenta given in Eq. (7) replaced with the transformed momenta

$$\vec{\pi}_r = \vec{p}_r - e_r(\vec{A}_r - \vec{A}_{\text{c.m.}}) - \frac{m_r}{M}\sum_s e_s\vec{A}_s \,, \tag{27}$$

for which I now use the same symbol. In Eq. (27) $\vec{A}_{\text{c.m.}}$ is defined by the equation

$$\vec{A}_{\text{c.m.}} = \vec{A}(\vec{R}_{\text{c.m.}}) = \tfrac{1}{2}\vec{B}\times\vec{R}_{\text{c.m.}} \,. \tag{28}$$

The result (27) is the same as the corresponding result for atoms,[5] and consequently the unitary transformation gives a molecular Hamiltonian which has the same form as the atomic one. As a result, when this molecular Hamiltonian is reduced to nonrelativistic form using the methods of Ref. 5, one obtains a nonrelativistic molecular Hamiltonian which has the same form as the atomic one:

$$\mathcal{H} = \sum_r m_r + \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 + \cdots \,, \tag{29}$$

$$\mathcal{H}_0 = \sum_r (\pi_r^2/2m_r) + \sum_{r<s} (e_r e_s/r_{rs}) \,, \tag{30}$$

$$\mathcal{H}_1 = -\sum_r (\pi_r^4/8m_r^3) \,, \tag{31}$$

$$\mathcal{H}_2 = -\sum_r \sum_{s\neq r} (\pi e_r e_s/2m_r^2)(g_r - 1)\delta^3(\vec{r}_{rs}) \,, \tag{32}$$

$$\mathcal{H}_3 = -\sum_r \sum_{s\neq r} \frac{e_r e_s}{2m_r^2}(g_r - 1)r_{rs}^{-3}\vec{S}_r\cdot(\vec{r}_{rs}\times\vec{\pi}_r) \,, \tag{33}$$

$$\mathcal{H}_4 = \sum_r \sum_{s\neq r} (e_r e_s/2m_r m_s)g_r r_{rs}^{-3}\vec{S}_r\cdot(\vec{r}_{rs}\times\vec{\pi}_s) \,, \tag{34}$$

$$\mathcal{H}_5 = -\sum_r (e_r/2m_r) g_r \vec{S}_r \cdot \vec{B}[1-(\pi_r^2/2m_r^2)]$$

$$-\sum_r (e_r/4m_r^3)(g_r-2)\vec{S}_r \cdot (\pi_r^2 \overleftrightarrow{1} - \vec{\pi}_r\vec{\pi}_r)\cdot\vec{B}\ , \qquad (35)$$

$$\mathcal{H}_6 = -\sum_{r<s} \frac{e_r e_s}{2m_r m_s}[r_{rs}^{-1}\vec{\pi}_r\cdot\vec{\pi}_s + \vec{r}_{rs}(r_{rs}^{-3}\vec{r}_{rs}\cdot\vec{\pi}_r)\cdot\vec{\pi}_s], \qquad (36)$$

$$\mathcal{H}_7 = -\sum_{r<s}\frac{e_r e_s}{4m_r m_s} g_r g_s [\tfrac{8}{3}\pi \vec{S}_r\cdot\vec{S}_s \delta^3(\vec{r}_{rs})$$

$$+ r_{rs}^{-5}(3\vec{S}_r\cdot\vec{r}_{rs}\vec{S}_s\cdot\vec{r}_{rs} - \vec{S}_r\cdot\vec{S}_s r_{rs}^2)]\ , \qquad (37)$$

where

$$g_r \mu_{0r} = 2(e_r/2m_r + \kappa_r) \qquad (38)$$

defines the $g$ factor of particle $r$; for an electron $\mu_{0r}$ is taken to be the negative of the Bohr magneton $\mu_B = e/2m_e$ (the charge on the electron is defined to be $-e$, which makes the charge $e$, the Bohr magneton $\mu_B$, and electron $g$ factor $g_e$ all positive quantities).

Physical interpretations for the terms appearing in the reduced Hamiltonian have been given in a number of places.[29] It has been shown recently that, except for the "Darwin" term $\mathcal{H}_2$, all of the terms (30)–(37) can be derived using entirely classical electrodynamics.[30-32]

The theory which has been presented to this point is apparently applicable to any diatomic molecule and can be readily generalized to include polyatomics. From now on, however, the development will be directed specifically toward the calculation of the electron spin $g$ factors for the $^2\Sigma$ ground states of $H_2^+$ and its isotopic relatives. To that end I will select the terms of the nonrelativistic Hamiltonian which contribute to the $g$ factors of $\Sigma$ states and write them out for a one-electron molecule. Such a selection must include terms which contribute in both first- and second-order perturbation theory.[33] The latter class of terms does not contribute in the atomic case but does contribute in the case of a molecule due to the departure from spherical symmetry. At the same time numerous nuclear motional terms, which give contributions of relative order $\alpha^2 m_e/M \approx 0.03$ ppm and of higher orders and hence are much too small to be detected experimentally at the present time, are neglected. The resulting Hamiltonian, correct to order $\alpha^3\mu_B B$, is written for the center-of-mass frame ($\vec{P}_{\text{c.m.}} = \vec{R}_{\text{c.m.}} = 0$)

$$\mathcal{H} = \mathcal{H}_0^{(0)} + \mathcal{H}^{(1)}\ , \qquad (39)$$

where

$$\mathcal{H}_0^{(0)} = \frac{p_A^2}{2M_A} + \frac{p_B^2}{2M_B} + \frac{p_e^2}{2m_e} - \frac{Z_A e^2}{r_{eA}} - \frac{Z_B e^2}{r_{eB}} + \frac{Z_A Z_B e^2}{R}\ , \qquad (40)$$

with $R \equiv |\vec{R}_{BA}|$,

$$\mathcal{H}^{(1)} = \frac{e}{2m_e}\vec{L}_{eC}\cdot\vec{B} \qquad (41a)$$

$$+\frac{e^2}{2m_e^2}(g_e-1)\vec{S}\cdot\left(Z_A\frac{\vec{L}_{eA}}{r_{eA}^3} + Z_B\frac{\vec{L}_{eB}}{r_{eB}^3}\right) \qquad (41b)$$

$$+\frac{e^3}{2m_e^2}(g_e-1)\vec{S}\cdot\left(Z_A\frac{\vec{r}_{eA}\times\vec{A}_{eC}}{r_{eA}^3} + Z_B\frac{\vec{r}_{eB}\times\vec{A}_{eC}}{r_{eB}^3}\right) \qquad (41c)$$

$$+\frac{e}{2m_e} g_e \vec{S}\cdot\vec{B}\left(1-\frac{p_{eC}^2}{2m_e^2}\right) \qquad (41d)$$

$$+\frac{e}{4m_e^3}(g_e-2)\vec{S}\cdot(p_{eC}^2\overleftrightarrow{1} - \vec{p}_{eC}\vec{p}_{eC})\cdot\vec{B}\ , \qquad (41e)$$

with

$$\vec{L}_{eC} = \vec{r}_{eC}\times\vec{p}_{eC}\ , \qquad (42a)$$

$$\vec{L}_{eA} = \vec{r}_{eA}\times\vec{p}_{eC}\ , \qquad (42b)$$

$$\vec{L}_{eB} = \vec{r}_{eB}\times\vec{p}_{eC}\ , \qquad (42c)$$

and where the charges on the nuclei have been written as $Z_A e$ and $Z_B e$. The term $\mathcal{H}_0^{(0)}$ in the Hamiltonian arises from the magnetic-field-independent part of $\mathcal{H}_0$ which has been given previously in Eq. (30). The term $\mathcal{H}^{(1)}$ contains several contributing terms as shown in Eq. (41). The first term (41a) is the usual orbital Zeeman effect, and comes from the magnetic-field-dependent part of $\mathcal{H}_0$ in Eq. (30). The second term (41b) is the usual spin-orbit coupling term and comes from $\mathcal{H}_3$ in Eq. (33). The third term (41c) also comes from $\mathcal{H}_3$ in Eq. (33) and may be interpreted as a spin-orbit coupling term in which the magnetic-field-dependent part of the mechanical momentum [Eq. (27)] appears. The fourth and fifth terms (41d) and (41e) come from $\mathcal{H}_5$ in Eq. (35). The fourth term may be interpreted as the usual spin Zeeman effect with a relativistic mass correction,[20,24,31] and the fifth term has a similar appearance but has no simple physical interpretation in terms of the relativistic mass. According to the classical treatment[30-32] of the Zeeman effect the sum of the terms (41d) and (41e) arises from just the interaction of the electron-spin magnetic moment with the magnetic field experienced in the electron's rest frame. The more complicated expression which results when this interaction is expressed in the laboratory frame (or in the molecular frame) is due to three relativistic effects: (i) the difference in time scales in the two frames, (ii) the Lorentz transformation of the magnetic field between the two frames, and (iii) the Thomas precession of the electron spin due to the acceleration of the electron produced by the magnetic field. It is interesting to note in this regard that the quantity $\vec{S}$ is to be interpreted as the electron spin *in its own rest* *frame*, even though the Hamiltonian (29) is written for the laboratory or molecular frame and not for the electron rest frame. As a final remark in this discussion of the Hamiltonian (39), I call the reader's attention to the result that the angular momentum $\vec{L}_{eC}$ which appears in (41a) and is defined in (42a) represents the orbital angular momentum of the electron about the nuclear center of mass, whereas the angular momenta $\vec{L}_{eA}$ and $\vec{L}_{eB}$ which appear in the spin-orbit coupling term (41b) represent the orbital angular momenta about the nuclei $A$ and $B$, respectively, as shown in Eqs. (42b) and (42c).

Having now constructed the Hamiltonian appropriate to the electronic Zeeman effect for the ground states of $H_2^+$-like molecules, one is faced with the problem of finding the $g$ values. This can be accomplished in a most satisfactory way by using Pryce's[22] modified degenerate perturbation theory to construct an effective Hamiltonian which operates entirely within the linear manifold associated with the ground electronic state. In the present case the unperturbed states $\psi_n^{(0)}(\vec{R}_{BA}, \vec{r}_{eC})$ are eigenstates of the unperturbed Hamiltonian (40); the perturbation $\mathcal{H}^{(1)}$ is given in (41a)–(41e); the ground state $\psi_0^{(0)}$ is orbitally nondegenerate but possesses spin and rotational degeneracies. Using this method, one obtains the effective Zeeman Hamiltonian

$$\mathcal{H}^{\text{eff}} = \frac{e}{2m_e} g_e \vec{S}\cdot\vec{B}\left(1 - \frac{\langle\psi_0^{(0)}|p_{eC}^2|\psi_0^{(0)}\rangle}{2m_e^2}\right) \tag{43a}$$

$$+\frac{e}{4m_e^3}(g_e-2)\vec{S}\cdot\langle\psi_0^{(0)}|p_{eC}^2\overleftrightarrow{1} - \vec{p}_{eC}\vec{p}_{eC}|\psi_0^{(0)}\rangle\cdot\vec{B} \tag{43b}$$

$$+\frac{e}{2m_e}(g_e-1)\vec{S}\cdot \sum_{X=A,B} Z_X\left(\frac{e^2}{2m_e}\langle\psi_0^{(0)}|\frac{\vec{r}_{eC}\cdot\vec{r}_{eX}\overleftrightarrow{1} - \vec{r}_{eC}\vec{r}_{eX}}{r_{eX}^3}|\psi_0^{(0)}\rangle \right.$$
$$\left. + 4\left(\frac{e}{2m_e}\right)^2 \sum_{n\neq 0} \frac{\langle\psi_0^{(0)}|r_{eX}^{-3}\vec{L}_{eX}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\vec{L}_{eC}|\psi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}}\right)\cdot\vec{B}\,. \tag{43c}$$

Notice that the second-order term in (43c) arises as a cross term between the orbital Zeeman term (41a) and the spin-orbit coupling term (41b); it is this term alone which appears in Pryce's theory of the $g$ tensor and in many subsequent formulations. It was Stone[23] who first pointed out that the first term of (43c) should also be present and that its presence makes (43c) gauge invariant. I have pointed out previously[20] that the sum of the two terms inside the large parentheses in (43c) give precisely Ramsey's expression[25] for the nuclear magnetic shielding tensor $\overleftrightarrow{\sigma}_X$ of nucleus $X$ in the molecule. (A derivation of Ramsey's expression with the present formalism is given in Appendix A.) Hence a theoretical calculation of (43c) is precisely equivalent to a theoretical calculation of the nuclear magnetic shielding tensor for each nucleus in the molecule, and suggests a fundamental relationship between the $g$ tensor and the nuclear magnetic shielding tensor.[20] From now on I will use the symbol $\overleftrightarrow{\sigma}_X$ to represent the terms between the large parentheses in (43c). To obtain an expression for the $g$ tensor itself, one may note that the effective Hamiltonian (43a), (43b), and (43c) can also be written in the form of Eq. (2). The expression for the $g$ tensor is then

$$\overleftrightarrow{g} = g_e\left(1 - \frac{\langle\psi_0^{(0)}|p_{eC}^2|\psi_0^{(0)}\rangle}{2m_e^2}\right)\overleftrightarrow{1} \tag{44a}$$

$$+\frac{1}{2m_e^2}(g_e-2)\langle\psi_0^{(0)}|p_{eC}^2\overleftrightarrow{1} - \vec{p}_{eC}\vec{p}_{eC}|\psi_0^{(0)}\rangle \tag{44b}$$

$$+(g_e-1)\sum_{X=A,B} Z_X\overleftrightarrow{\sigma}_X\,. \tag{44c}$$

This expression for the $g$ tensor is apparently accurate to order $\alpha^3$. The first term in (44) is an isotropic correction to the free-electron $g$ factor arising from the "relativistic mass increase" of the electron[20,24,31]: the correction is of order $\alpha^2$. The second term is a small anisotropic correction of order $\alpha^3$. The third term arises from the spin-orbit coupling terms (41b) and (41c); it is also anisotropic and contains corrections of orders $\alpha^2$ and $\alpha^3$.

For the subsequent calculations on $H_2^+$, $HD^+$, and $D_2^+$ the above expression for the $g$ tensor is simplified by neglecting the contributions of order $\alpha^3$ $\approx 0.4$ ppm. The small numerical factors contained in the $\alpha^3$ terms reduce their magnitudes even further, and consequently it seems improbable that experiments will be sensitive enough to detect their presence for some time. The resulting expression, correct to order $\alpha^2$, can then be written

$$\frac{\overleftrightarrow{\mathrm{g}}}{g_e}=\left(1-\frac{\langle\psi_0^{(0)}\,|\,T_e\,|\psi_0^{(0)}\rangle}{m_e c^2}\right)\overleftrightarrow{1}+\overleftrightarrow{\sigma}\ , \tag{45}$$

where $T_e = p_{eC}^2/2m_e$ is the electron nonrelativistic kinetic energy operator and $\overleftrightarrow{\sigma}$ is the nuclear magnetic shielding tensor for either of the two nuclei in the molecule. The factor $c^2$ has been inserted into Eq. (45) to show explicitly the ratio of the two energies $T_e$ and $m_e c^2$.

## III. NUMERICAL CALCULATIONS AND RESULTS

The result of the preceding theoretical treatment, Eq. (45), is used to compute the components of the $g$ tensors for $H_2^+$, $HD^+$, and $D_2^+$. The computations are performed in a coordinate frame which is fixed relative to the internuclear axis. The $z$ axis is taken to be along the internuclear axis and directed from nucleus $A$ toward nucleus $B$. There are two unique components of the $g$ tensor, namely $g_\perp \equiv g_{xx} = g_{yy}$ and $g_\parallel \equiv g_{zz}$. The adiabatic approximation,[34,35] which should be excellent for these calculations, is made. According to this approximation a molecular wave function, i.e., an eigenfunction of $\mathcal{H}_0^{(0)}$ in Eq. (40) is written

$$\psi_n^{(0)}(\vec{\mathrm{R}}_{BA},\vec{\mathrm{r}}_{eC})=\psi_{e,n}^{(0)}(R,\vec{\mathrm{r}}_{eC})\mathrm{R}^{-1}\varphi_{vN}(R)F_n(\vec{\mathrm{R}}_{BA}/R)\ , \tag{46}$$

where the electronic wave function $\psi_{e,n}^{(0)}$ is a function of the electronic coordinates $\vec{\mathrm{r}}_{eC}$ and depends parametrically upon the internuclear distance $R$, where $\varphi_{vN}(R)$ is the vibrational-rotational (VR) wave function and depends on the vibrational quantum number $v$ and on the quantum number $N$ representing the total orbital angular momentum of the molecule, and where $F_n$ describes the orientation of the molecule with respect to the laboratory frame and contains the dependence upon the rotational and spin quantum numbers. Within the adiabatic approximation a molecular property is calculated for an individual VR state by first calculating the property as a function of $R$ using the electronic wave function, and then averaging this property over the VR wave function $\varphi_{vN}$.[36]

At this point it is convenient to switch to Hartree atomic units, which are commonly used for molecular calculations. In this system of units $\hbar = m_e = e = 1$ and $c = \alpha^{-1}$ is the speed of light. The Schrödinger equation for the electronic wave function is written for $H_2^+$

$$\mathcal{H}_e^{(0)}\psi_{e,n}^{(0)}=E_{e,n}(R)\psi_{e,n}^{(0)} \tag{47}$$

with

$$\mathcal{H}_e^{(0)}=\tfrac{1}{2}p_{eC}^2-r_{eA}^{-1}-r_{eB}^{-1}\ , \tag{48}$$

and that for the VR wave function becomes

$$\frac{1}{2\mu}\frac{d^2\varphi_{vN}}{dR^2}+V(R)\varphi_{vN}=E_{vN}\varphi_{vN} \tag{49}$$

with

$$V(R)=E_{e,n}(R)+R^{-1}+N(N+1)(2\mu R^2)^{-1}+\gamma(R)\ . \tag{50}$$

In the last two equations $\mu$ is the nuclear reduced mass

$$\mu=M_A M_B(M_A+M_B)^{-1} \tag{51}$$

and $\gamma(R)$ is an adiabatic correction[34,35] to $V(R)$. It is well known that Eq. (47) is separable in prolate spheroidal variables $\lambda$, $\mu$, $\varphi$ and that consequently very accurate wave functions $\psi_{e,n}^{(0)}(R,\lambda,\mu,\varphi)$ can be obtained.[26,37] For the present work the very accurate ground-state wave function obtained by Hunter and Pritchard[26] is used. This wave function has the form

$$\psi_e^{(0)}=(2\pi)^{-1/2}\Lambda(\lambda)M(\mu)\ , \tag{52}$$

where

$$\Lambda(\lambda)=(\lambda+1)^{\sigma}e^{-p\lambda}\sum_t g_t\left(\frac{\lambda-1}{\lambda+1}\right)^t\ , \tag{53}$$

where

$$M(\mu)=\sum_{s\text{ even}} f_s P_s(\mu) \tag{54}$$

and where the subscript 0 on $\psi_{e,0}^{(0)}$ has been dropped; from now on it will be understood that $\psi_e^{(0)}$ denotes the ground state. The reader is referred to Refs. 26 and 37 for the meanings of the symbols in Eqs. (53) and (54).

The components of the $g$ tensor computed as functions of $R$, are, from Eq. (45),

$$\frac{g_\perp(R)}{g_e}=1-\alpha^2\langle\psi_e^{(0)}|\,T_e\,|\psi_e^{(0)}\rangle+\sigma_\perp\ , \tag{55}$$

$$\frac{g_\parallel(R)}{g_e}=1-\alpha^2\langle\psi_e^{(0)}|\,T_e\,|\psi_e^{(0)}\rangle+\sigma_\parallel\ . \tag{56}$$

The kinetic energy integral and the parallel component of the nuclear magnetic shielding $\sigma_\parallel$ are computed using only the zero-order electronic wave function $\psi_e^{(0)}$. The perpendicular component of the nuclear magnetic shielding tensor consists of two terms

$$\sigma_\perp=\sigma_\perp^{(1)}+\sigma_\perp^{(2)} \tag{57}$$

the first of which is computed using $\psi_e^{(0)}$ and the second of which requires a knowledge of the first-order wave function for the molecule in the presence of a magnetic field $\vec{\mathrm{B}}$ applied perpendicular to the internuclear axis. According to Ramsey's theory[25] we have

$$\sigma_\parallel(R)=\sigma_{zz}(R)=\tfrac{1}{2}\alpha^2\langle\psi_e^{(0)}|r_{eA}^{-3}(x_{eA}^2+y_{eA}^2)|\psi_e^{(0)}\rangle\ , \tag{58}$$

$$\sigma_\perp^{(1)}(R)=\sigma_{xx}^{(1)}(R)=\tfrac{1}{2}\alpha^2\langle\psi_e^{(0)}|r_{eA}^{-3}(y_{eA}y_{eC}+z_{eA}z_{eC})|\psi_e^{(0)}\rangle\ , \tag{59}$$

and

$$\sigma_\perp^{(2)}(R)=\sigma_{xx}^{(2)}(R)=(2\alpha/B)\langle\psi_e^{(1)}|r_{eA}^{-3}L_{xeA}|\psi_e^{(0)}\rangle\ , \qquad (60)$$

where the first-order wave function $\psi_e^{(1)}$ satisfies the inhomogeneous equation

$$(\mathcal{H}_e^{(0)}-E_e^{(0)})\psi_e^{(1)}+\tfrac{1}{2}\alpha BL_{xeC}\psi_e^{(0)}=0\ . \qquad (61)$$

Note that $\sigma_\perp^{(1)}(R)$ and $\sigma_\perp^{(2)}(R)$ correspond, respectively, to the first and second terms within the large parentheses of Eq. (43c).

The kinetic energy integral and the shielding integrals in Eqs. (58) and (59) are computed in a straightforward manner by transforming the operators to prolate spheroidal coordinates. The kinetic energy integral can be obtained most easily by using the tabulated values[26] for $E_e$ and the relation

$$\langle\psi_e^{(0)}|T_e|\psi_e^{(0)}\rangle=E_e+2\langle\psi_e^{(0)}|r_{eA}^{-1}|\psi_e^{(0)}\rangle \qquad (62)$$

which follows from Eqs. (47) and (48) and from the symmetry of the homonuclear diatomic molecule. Each of the integrals contains a trivial integration over $\varphi$, an integration over $\mu$ which is done analytically, and a remaining integration over $\lambda$ which is performed using Gaussian quadrature techniques. Some care is required in computing the integral appearing in Eq. (59) because the integrand contains an (integrable) logarithmic singularity of the form $\ln(\lambda-1)$. This problem was handled by isolating those specific terms in the integrand containing the $\ln(\lambda-1)$ factor and by evaluating their contribution to the total integral by means of a numerical quadrature technique designed particularly for this type of integral.[38] The remaining singularity-free integrals were computed using a combination of Gauss-Legendre and Gauss-Leguerre quadratures.[39] Since the singularity appears in the integral for the operator $z_{eA}/r_{eA}^3$, which may be separated from the integrand in Eq. (59) using the relation $z_{eC}=z_{eA}-\frac{1}{2}R$, one can use the virial theorem to obtain the result

$$\langle\psi_e^{(0)}|r_{eA}^{-3}z_{eA}|\psi_e^{(0)}\rangle=-2R^{-1}(E_e+\langle\psi_e^{(0)}|r_{eR}^{-1}|\psi_e^{(0)}\rangle) \qquad (63)$$

and use this result to check the previous integration method. In all cases agreement was found to five or six significant figures. All computations were performed on a Hewlett-Packard 3000 computer in double precision arithmetic.

In order to obtain the first-order wave function $\psi_e^{(1)}$ a variation perturbation scheme was used to solve Eq. (61). A basis set was carefully chosen to eliminate singularities in the differential equation and $\psi_e^{(1)}$ was expanded in terms of this basis

$$\psi_e^{(1)}(R,\lambda,\mu,\varphi)=\sin\varphi\sum_{nl}A_{nl}(R)f_n(R,\lambda)P_l^1(\mu)\ , \qquad (64)$$

where

$$f_n(R,\lambda)=-\tfrac{1}{4}(2\pi)^{-1/2}i\alpha BR^2(\lambda^2-1)^{1/2}$$
$$\times(\lambda+1)^{\sigma}e^{-p\lambda}\left(\frac{\lambda-1}{\lambda+1}\right)^n\ , \qquad (65)$$

where $P_l^1(\mu)$ are associated Legendre functions of order one and with $l$ restricted to the even integers, and where the quantities $\sigma$ and $p$ have the same values as they do in the expression for $\psi_e^{(0)}$. The coefficients $A_{nl}(R)$ were found by minimizing the quantity

$$W=\langle\psi_e^{(0)}|\mathcal{H}^{(1)}|\psi_e^{(1)}\rangle+\langle\psi_e^{(1)}|\mathcal{H}^{(1)}|\psi_e^{(0)}\rangle$$
$$+\langle\psi_e^{(1)}|\mathcal{H}_e^{(0)}-E_e|\psi_e^{(1)}\rangle \qquad (66)$$

with $\mathcal{H}^{(1)}=\frac{1}{2}\alpha BL_{xeC}$. The resulting set of inhomogeneous simultaneous equations for the coefficients $A_{nl}$ was solved by Gaussian elimination.[40] The size of the basis set for a given value of $R$ was chosen according to the criterion that the shielding term $\sigma_\perp^{(2)}$ not change in the fourth decimal place (when expressed in ppm) when additional basis functions are added. The coefficients obtained when $R=2.00$, which is very close to the equilibrium internuclear distance, are given in Table I. The resulting magnetic properties, including the diamagnetic susceptibility components, $\chi_\perp$, $\chi_\parallel$ which can be computed from the same wave function, are presented in Table II and compared with previous results.[20,41] The present results for the second-order properties in Table II are shown for both the 15-term expansion whose coefficients are given in Table I and also (the value in parentheses) for a first-order wave function with the single term $n=0$, $l=2$, in order to indicate the rapidity of convergence of the properties. The present results confirm the previous results[20,41] for the first-order properties and represent a significant improvement in the second-order properties, par-

TABLE I. Expansion coefficients for the first-order wave function with $R=2.00$.

| $n$ | $l$ | $A_{nl}$ |
|---|---|---|
| 0 | 2 | −0.341 527 |
| 0 | 4 | −0.012 394 |
| 0 | 6 | −0.000 191 |
| 1 | 2 | 0.006 459 |
| 1 | 4 | −0.000 180 |
| 1 | 6 | −0.000 007 |
| 2 | 2 | 0.021 477 |
| 2 | 4 | 0.000 680 |
| 2 | 6 | 0.000 009 |
| 3 | 2 | −0.005 455 |
| 3 | 4 | −0.000 203 |
| 3 | 6 | −0.000 003 |
| 4 | 2 | 0.023 427 |
| 4 | 4 | 0.000 785 |
| 4 | 6 | 0.000 011 |

TABLE II. Magnetic properties of $H_2^+$ for $R = 2.00$ a.u.

| Property[a] | Present result | Previous result |
|---|---|---|
| $\chi_\perp^{(1)}$ | −0.4382 | −0.4382 [b] |
| $\chi_\perp^{(2)}$ | 0.0378 (0.0375) [c] | 0.0314 [b] |
| $\chi_\parallel$ | −0.3209 | −0.3209 [b] |
| $\sigma_\perp^{(1)}$ | 9.8852 | 9.89 [b] |
| $\sigma_\perp^{(2)}$ | 1.1142 (1.072) [c] | 0.642 [b] |
| $\sigma_\parallel$ | 12.2899 | 12.29 [b] |
| $g_\perp/g_e - 1$ | −21.0610 (−21.103) [c] | −21.56 [d] |
| $g_\parallel/g_e - 1$ | −19.7705 | −19.80 [d] |

[a] Magnetic susceptibility $\chi$ given in units of $\alpha^2 a_0^3$, where $a_0$ is the Bohr radius. The other properties are unitless and should be multiplied by $10^{-6}$.

[b] Reference 41.

[c] Numbers in parentheses calculated with only one term in the summation in Eq. (64).

[d] Reference 20.

ticularly in $\sigma_\perp^{(2)}$. As a consequence, the value of $g_\perp/g_e$ at $R = 2.00$ is improved by 0.5 ppm. Similar calculations were performed for a range of $R$ values between zero and infinity, and the results are given in Table III. All of these results are expected to be computationally accurate to three or four decimal places. The values at $R = 0$ and $R \to \infty$ correspond to a singly ionized helium atom and to a hydrogen atom, respectively, and are calculated from the expression for the $g$ value of an hydrogenic atom,[2-3] which to order $\alpha^2$ is

$$g/g_e = 1 - \tfrac{1}{3}(\alpha Z)^2 \ . \tag{67}$$

As expected, the $g$ values for $H_2^+$ vary with internuclear distance in a continuous fashion between these two limits. In fact, this variation of $g$ vs $R$ for $H_2^+$ must contain information regarding the effect of chemical bond formation, since $H_2^+$ can be thought of as the chemical combination of a bare proton with a hydrogen atom, the bond being formed as the two nuclei are brought sufficiently close together from an initially large distance apart.

TABLE III. $g$ values and related properties of $H_2^+$ vs internuclear distance.[a]

| $R$ (a.u.) | $\sigma_\perp^{(1)}$ | $\sigma_\perp^{(2)}$ | $\sigma_\parallel$ | $\alpha^2 \langle T_e \rangle$ | $1 - g_\perp/g_e$ | $1 - g_\parallel/g_e$ |
|---|---|---|---|---|---|---|
| 0.00 | 35.5009 | 0.0000 | 35.5009 | 106.5027 | 71.0018 | 71.0018 |
| 0.015625 | 35.4656 | 0.0000 | 35.4717 | 106.4029 | 70.9373 | 70.9312 |
| 0.125 | 33.8302 | 0.0052 | 34.1107 | 101.7712 | 67.9358 | 67.6605 |
| 0.250 | 30.6794 | 0.0369 | 31.4552 | 92.8141 | 62.0978 | 61.3589 |
| 0.500 | 24.5014 | 0.1801 | 26.1173 | 75.1200 | 50.4385 | 49.0027 |
| 0.750 | 19.8341 | 0.3698 | 21.9437 | 61.6120 | 41.4081 | 39.6683 |
| 1.00 | 16.4794 | 0.5601 | 18.8413 | 51.8002 | 34.7607 | 32.9589 |
| 1.25 | 14.0462 | 0.7331 | 16.5165 | 44.6091 | 29.8298 | 28.0926 |
| 1.50 | 12.2504 | 0.8833 | 14.7438 | 39.2446 | 26.1109 | 24.5008 |
| 1.75 | 10.9044 | 1.0101 | 13.3695 | 35.1784 | 23.2639 | 21.8089 |
| 2.00 | 9.8852 | 1.1142 | 12.2899 | 32.0604 | 21.0610 | 19.7705 |
| 2.25 | 9.1100 | 1.1968 | 11.4340 | 29.6541 | 19.3473 | 18.2201 |
| 2.50 | 8.5220 | 1.2590 | 10.7517 | 27.7958 | 18.0148 | 17.0441 |
| 2.75 | 8.0809 | 1.3018 | 10.2071 | 26.3689 | 16.9862 | 16.1618 |
| 3.00 | 7.7574 | 1.3258 | 9.7735 | 25.2883 | 16.2051 | 15.5148 |
| 3.50 | 7.3798 | 1.3213 | 9.1631 | 23.9228 | 15.2217 | 14.7597 |
| 4.00 | 7.2627 | 1.2536 | 8.8047 | 23.3302 | 14.8139 | 14.5255 |
| 4.50 | 7.3189 | 1.1348 | 8.6198 | 23.2572 | 14.8035 | 14.6374 |
| 5.00 | 7.4801 | 0.9818 | 8.5502 | 23.5106 | 15.0487 | 14.9604 |
| 6.00 | 7.9177 | 0.6482 | 8.5899 | 24.4254 | 15.8595 | 15.8355 |
| 7.00 | 8.3063 | 0.3728 | 8.6966 | 25.3094 | 16.6303 | 16.6128 |
| 8.00 | 8.5650 | 0.1945 | 8.7821 | 25.9125 | 17.1530 | 17.1304 |
| 9.00 | 8.7130 | 0.0953 | 8.8332 | 26.2596 | 17.4513 | 17.4264 |
| 10.00 | 8.7910 | 0.0449 | 8.8595 | 26.4419 | 17.6060 | 17.5824 |
| 11.00 | 8.8305 | 0.0207 | 8.8717 | 26.5330 | 17.6818 | 17.6613 |
| 12.00 | 8.8502 | 0.0095 | 8.8768 | 26.5776 | 17.7179 | 17.7008 |
| 14.00 | 8.8654 | 0.0021 | 8.8791 | 26.6102 | 17.7427 | 17.7311 |
| 16.00 | 8.8703 | 0.0006 | 8.8785 | 26.6190 | 17.7481 | 17.7405 |
| 18.00 | 8.8720 | 0.0002 | 8.8778 | 26.6220 | 17.7498 | 17.7442 |
| 22.00 | 8.8740 | 0.0001 | 8.8767 | 26.6241 | 17.7500 | 17.7474 |
| ∞ | 8.8752 | 0.0000 | 8.8752 | 26.6257 | 17.7504 | 17.7504 |

[a] All numerical values given in the table except $R$ are unitless and should be multiplied by $10^{-6}$.

In Fig. 1 the primary effect of chemical bond formation can be seen clearly. In this figure the negative of the shift of the average $g$ value of $H_2^+$ relative to the hydrogen atom

$$\frac{\Delta g_{\mathrm{av}}}{g_e}=\frac{g_{\mathrm{av}}-g_{\mathrm{H\ atom}}}{g_e} \tag{68}$$

is plotted (solid line) as a function of $R$, where

$$g_{\mathrm{av}}=\tfrac{1}{3}(2g_\perp+g_\parallel) \tag{69}$$

is the average value of the $g$ tensor for $H_2^+$, and where $g_{\mathrm{H\ atom}}/g_e=1-17.75\times10^{-6}$. On the same graph the shift of the electron's kinetic energy in $H_2^+$ relative to the hydrogen atom

$$\alpha^2\langle\Delta T_e\rangle=\alpha^2(\langle T_e\rangle-\langle T_e\rangle_{\mathrm{H\ atom}}) \tag{70}$$

is also plotted (dotted line). The graph clearly shows that the negative of the $g$ shift and the electronic kinetic energy shift, which is proportional to the shift in the relativistic mass of the electron, vary with internuclear distance in the same manner, and in fact are nearly equal for much of the range shown. The difference in the curves gives the small, but by no means negligible, chemical shift in $\sigma_{\mathrm{av}}$ [see Eq. (45)]. The variation of the electron's kinetic energy with internuclear distance and its relation to the chemical bond are understood quite well.[42] Hence most of the variation of the $g$ tensor with $R$ may be understood on a similar basis. At the equilibrium internuclear distance $R=2.00$ a.u. one finds that the relativistic

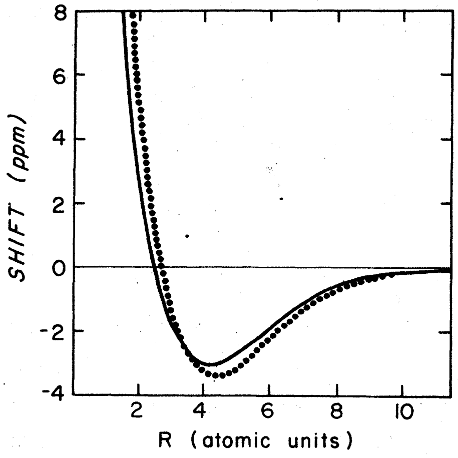

FIG. 1. Effect of chemical bond formation on $g$ values. Shifts in $-g_{\mathrm{av}}/g_e$ (solid curve) and in $\alpha^2\langle T_e\rangle$ (dotted curve) for $H_2^+$ relative to H atom are plotted vs internuclear distance $R$.

TABLE IV. $g$ values for vibrational-rotational states of $H_2^+$.[a]

| $v$ | $N$ | $1-\langle g_\perp/g_e\rangle_{vN}$ | $1-\langle g_\parallel/g_e\rangle_{vN}$ | $v$ | $N$ | $1-\langle g_\perp/g_e\rangle_{vN}$ | $1-\langle g_\parallel/g_e\rangle_{vN}$ |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 20.776 | 19.526 | 3 | 0 | 19.209 | 18.206 |
| 0 | 1 | 20.756 | 19.508 | 3 | 1 | 19.193 | 18.191 |
| 0 | 2 | 20.717 | 19.472 | 3 | 2 | 19.161 | 18.163 |
| 0 | 3 | 20.658 | 19.419 | 3 | 3 | 19.113 | 18.120 |
| 0 | 4 | 20.580 | 19.348 | 3 | 4 | 19.051 | 18.064 |
| 0 | 6 | 20.374 | 19.160 | | | | |
| 0 | 8 | 20.105 | 18.917 | 4 | 0 | 18.773 | 17.848 |
| 0 | 10 | 19.785 | 18.628 | 4 | 1 | 18.758 | 17.835 |
| 0 | 12 | 19.424 | 18.304 | 4 | 2 | 18.728 | 17.808 |
| 0 | 14 | 19.033 | 17.956 | 4 | 3 | 18.684 | 17.770 |
| 0 | 16 | 18.623 | 17.593 | 4 | 4 | 18.626 | 17.718 |
| 0 | 18 | 18.203 | 17.224 | | | | |
| 0 | 20 | 17.781 | 16.857 | 6 | 0 | 18.025 | 17.252 |
| 0 | 26 | 16.573 | 15.833 | 8 | 0 | 17.446 | 16.817 |
| 0 | 30 | 15.872 | 15.268 | 10 | 0 | 17.043 | 16.547 |
| 0 | 35 | 15.191 | 14.769 | 12 | 0 | 16.829 | 16.457 |
| | | | | 14 | 0 | 16.832 | 16.574 |
| 1 | 0 | 20.210 | 19.044 | 16 | 0 | 17.093 | 16.940 |
| 1 | 1 | 20.191 | 19.027 | 18 | 0 | 17.615 | 17.573 |
| 1 | 2 | 20.154 | 18.993 | | | | |
| 1 | 3 | 20.099 | 18.944 | | | | |
| 1 | 4 | 20.027 | 18.878 | | | | |
| 2 | 0 | 19.688 | 18.604 | | | | |
| 2 | 1 | 19.671 | 18.588 | | | | |
| 2 | 2 | 19.636 | 18.557 | | | | |
| 2 | 3 | 19.585 | 18.511 | | | | |
| 2 | 4 | 19.518 | 18.451 | | | | |

[a] All numerical values in the table except those for $v$ and $N$ should be multiplied by $10^{-6}$.

TABLE V. $g$ values for vibrational-rotational states of $HD^+$.[a]

| $v$ | $N$ | $1-\langle g_\perp/g_e\rangle_{vN}$ | $1-\langle g_\parallel/g_e\rangle_{vN}$ | $v$ | $N$ | $1-\langle g_\perp/g_e\rangle_{vN}$ | $1-\langle g_\parallel/g_e\rangle_{vN}$ |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 20.817 | 19.562 | 3 | 0 | 19.429 | 18.388 |
| 0 | 1 | 20.802 | 19.548 | 3 | 1 | 19.417 | 18.377 |
| 0 | 2 | 20.772 | 19.521 | 3 | 2 | 19.392 | 18.355 |
| 0 | 3 | 20.728 | 19.480 | 3 | 3 | 19.355 | 18.321 |
| 0 | 4 | 20.669 | 19.427 | 3 | 4 | 19.306 | 18.278 |
| 0 | 6 | 20.511 | 19.283 | | | | |
| 0 | 8 | 20.303 | 19.094 | 4 | 0 | 19.032 | 18.060 |
| 0 | 10 | 20.052 | 18.867 | 4 | 1 | 19.020 | 18.049 |
| 0 | 20 | 18.389 | 17.384 | 4 | 2 | 18.997 | 18.028 |
| 0 | 30 | 16.606 | 15.858 | 4 | 3 | 18.962 | 17.997 |
| 0 | 40 | 15.240 | 14.798 | 4 | 4 | 18.916 | 17.957 |
| 1 | 0 | 20.321 | 19.139 | 6 | 0 | 18.331 | 17.493 |
| 1 | 1 | 20.307 | 19.126 | 8 | 0 | 17.756 | 17.046 |
| 1 | 2 | 20.279 | 19.100 | 10 | 0 | 17.308 | 16.719 |
| 1 | 3 | 20.237 | 19.062 | 12 | 0 | 16.995 | 16.520 |
| 1 | 4 | 20.182 | 19.012 | 14 | 0 | 16.827 | 16.458 |
| | | | | 16 | 0 | 16.821 | 16.551 |
| 2 | 0 | 19.859 | 18.748 | 18 | 0 | 17.006 | 16.828 |
| 2 | 1 | 19.846 | 18.736 | 20 | 0 | 17.403 | 17.318 |
| 2 | 2 | 19.819 | 18.712 | | | | |
| 2 | 3 | 19.780 | 18.676 | | | | |
| 2 | 4 | 19.728 | 18.629 | | | | |

[a] All numerical values except those for $v$ and $N$ should be multiplied by $10^{-6}$.

mass of the electron increases by 5.43 ppm and $\sigma_{av}$ by 2.55 ppm relative to the respective H-atom values. The result is a $g_{av}$ shift of $-2.88$ ppm for $H_2^+$ relative to H.

Now any experimental measurement of the $g$ values for $H_2^+$ will measure these quantities for an individual vibrational-rotational state or for a statistical distribution of VR states. In order to complete the calculation to find $g$ values for these quantum states one must average $g_\perp(R)$ and $g_\parallel(R)$ over the VR wave functions $\varphi_{vN}(R)$ as discussed in the first paragraph of this section. These functions, which are solutions to the differential equation (49), have been found along with the corresponding eigenvalues $E_{vN}$ by several workers.[34,35,43–46] In the present work the potential energy function $V(R)$ in Eq. (50) was constructed using the $E_e(R)$ values published by Wind[44] and the $\gamma(R)$ values published by Bishop and Wetmore,[34] and then Eq. (49) was solved for $\varphi_{vN}$ for several VR states using the Runge-Kutta method.[47] The corresponding $g$ values were then calculated by numerical integration using the trapezoid rule. Results for $H_2^+$ are presented in Table IV. Similar calculations were performed for $HD^+$ and for $D_2^+$ and the results of these calculations are presented, respectively, in Tables V and VI. In the case of the $H_2^+$ ground VR state $\varphi_{00}$ one finds that the shift in $g_{av}$ is $-2.61$ ppm relative to the H atom, which may be compared with the previous result $-2.88$ ppm for $R=2.00$.

The primary effect of the vibrational corrections to the $g$ values is illustrated in Fig. 2, where $g_{av}/g_e - 1$ is plotted as a function of internuclear distance and is represented by the heavy solid curve. The heavy horizontal dotted line represents the asymptotic atomic hydrogen value, $-17.75\times10^{-6}$. Also shown in the figure by two heavy horizontal bars are the values of $\langle g_{av}/g_e\rangle_{v0} - 1$ for the vibrational states $v=0$ and $v=18$ for $H_2^+$. The probability densities for these two states are plotted in the upper part of the figure, and the average values of the internuclear distance $\langle R\rangle_{v0}$ for the two states are indicated by vertical dotted lines. From the figure it can be seen that the major vibrational effect is to produce a $g$ value which is closely

TABLE VI. $g$ values for vibrational-rotational states of $D_2^+$.[a]

| $v$ | $N$ | $1-\langle g_\perp/g_e\rangle_{vN}$ | $1-\langle g_\parallel/g_e\rangle_{vN}$ |
|---|---|---|---|
| 0 | 0 | 20.865 | 19.603 |
| 1 | 0 | 20.455 | 19.253 |
| 2 | 0 | 20.068 | 18.924 |
| 10 | 0 | 17.737 | 17.032 |
| 20 | 0 | 16.834 | 16.575 |
| 24 | 0 | 17.287 | 17.178 |

[a] All numerical values except those for $v$ and $N$ should be multiplied by $10^{-6}$.

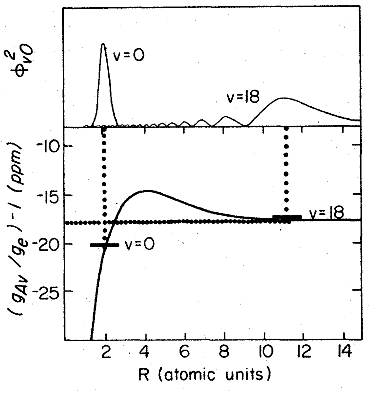

FIG. 2. Effect of vibrational corrections to $g$ values. The heavy solid curve shows variation of $g_{\text{av}}/g_e - 1$ vs internuclear distance $R$ for $H_2^+$; the asymptotic H-atom value is indicated by the horizontal heavy dotted line; values for the vibrational states $v=0$ and $v=18$ are shown by heavy horizontal bars. Probability densities for these two states are given at top of the figure (the values for the $v=0$ density have been reduced by $\frac{1}{2}$ for clarity). The vertical heavy dotted lines indicate the average value of $R$ for each state.

associated with the average value of $R$ for the vibrational state. Because of the asymmetry of the potential energy $V(R)$ about the equilibrium internuclear distance $R_e = 2.00$ a.u., the average value of $R$ increases with increasing vibrational quantum number $v$. Consequently the higher vibrational states have $g$ values corresponding to larger internuclear distances. This effect is further illustrated in Fig. 3, in which the values of $\langle g_{\text{av}}/g_e\rangle_{v0} - 1$ are plotted versus $\langle R\rangle_{v0}$ for several vibrational states; the values of $v$ for these states are written inside the open circles. The $g$ values are seen to lie along a curve which is very similar to the corresponding curve in Fig. 2. It may also be noticed that the Fig. 3 curve has been "damped" with respect to the Fig. 2 curve in the region between $R \approx 2$ and $R \approx 10$. This effect arises because the vibrational states with average values of $R$ in this region have probability densities which are large over a region where $g_{\text{av}}(R)$ is varying significantly and hence there is an averaging effect. It was found that not only the $H_2^+$ $g$ values, but also those for $HD^+$ and $D_2^+$ lie along essentially the same curve as long as one continues to plot states for which $N=0$. There is a similar effect for states with $N \neq 0$, except that each $N$ value generates a slightly different curve. The major effect of rotation on the $g$ value is hence effectively the same as that of vibration; due to centrifugal "stretching" of the chemical bond, the states with larger $N$ values have $g$ values which correspond to larger values of $R$.

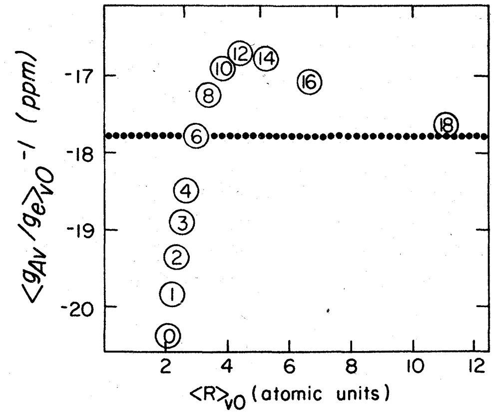

FIG. 3. $g$ values for vibrational states $H_2^+$ with rotational quantum number $N=0$. The variation of $\langle g_{\text{av}}/g_e\rangle_{v0} - 1$ vs average internuclear distance $\langle R\rangle_{v0}$ is shown. The values of the vibrational quantum number $v$ appear inside the open circles. The horizontal heavy dotted line indicates the value of $g/g_e - 1$ for the H atom $^2S$ ground state.

Finally, it is useful to incorporate the results of these calculations into the effective Zeeman spin Hamiltonian (2) written for the laboratory frame of reference in which the magnetic field $\vec{B}$ is taken to be along the $z$ axis. The result is[48]

$$\mathcal{H}^{\text{eff}} = g_{\text{av}}\mu_B B S_z + \tfrac{1}{3}\sqrt{2}\,(g_\perp - g_\parallel)\mu_B B(D^{(22)}S^{(10)})^{(12)}_{00}\,, \tag{71}$$

where $D$ and $S$ are spherical tensor operators. Matrix elements of the last term in Eq. (71) can be evaluated in terms of 3-$j$ and 9-$j$ symbols.[48] The first term in (71) will be dominant due to the larger value of $g_{\text{av}}$ compared to the anisotropy $g_\perp - g_\parallel$.

## IV. RELATIONSHIP TO THE ELECTRON SPIN-ROTATION TENSOR

An approximate relationship between the $g$ tensor and the electron spin-rotation tensor $\overleftrightarrow{d}$, which appears in the interaction

$$\mathcal{H}^{\text{eff}}_{\text{spin-rot}} = \vec{S}\cdot\overleftrightarrow{d}\cdot\vec{N}\,, \tag{72}$$

has been derived by Curl.[49] Such relationships between different magnetic properties are extremely useful because they provide consistency checks for experimental measurements of the different properties as well as for the corresponding theoretical calculations, and because they provide conceptual unifications for the theory. In this section I would like to point out a relationship between the spin-rotation tensor and the nuclear magnetic shielding tensor which is exact for a one-electron molecule and which may lead to useful approximations for a many-electron molecule. This relationship is expressed in Hartree atomic units as

$$\overleftrightarrow{d}^{(2)} = -\frac{g_e - 1}{\mu R^2}\sum_X Z_X \overleftrightarrow{\sigma}^{(2)}_X\,, \tag{73}$$

where $\vec{d}^{(2)}$ is the second-order part of the electron spin-rotation tensor and the summation is over all the nuclei in the molecule. The other quantities appearing in Eq. (73) have been defined previously in this paper. A derivation of (73) is given in Appendix B. The expression (73) for $\vec{d}^{(2)}$, when combined with the first-order contribution $\vec{d}^{(1)}$ and with Eq. (45), then gives a relationship between $\vec{d}$ and $\vec{g}$ which, although more complicated than Curl's expression, is exact for a one-electron system. For example, for $H_2^+$ Eq. (73) becomes, after terms of order $\alpha^3$ are neglected,

$$d_\perp^{(2)} = -(g_e/\mu R^2)\sigma_\perp^{(2)}, \qquad (74)$$

which for the equilibrium internuclear distance $R_e = 2.00$ gives the result

$$d_\perp^{(2)} = -6.075\times10^{-10}\ \text{a.u.} = -3.997\ \text{MHz} \qquad (75)$$

when the value for $\sigma_\perp^{(2)}$ given in Table III is used. This result is in excellent agreement with a recent calculation[50] of $d_\perp^{(2)}$ and in fact, the two calculations agree exactly to four significant figures if the nuclear mass correction used in Ref. 50 is taken into account. The first-order contribution at $R_e$ is

$$d_\perp^{(1)} = \frac{g_e\alpha^2}{2\mu R}\left\langle \psi_e^{(0)} \middle| \frac{z_{eA}}{r_{eA}^3} \middle| \psi_e^{(0)} \right\rangle$$
$$= 7.2674\times10^{-9}\ \text{a.u.} = 47.817\ \text{MHz} \qquad (76)$$

(without the nuclear mass correction). Hence we obtain for $d_\perp^{(1)} + d_\perp^{(2)}$ the value $d_\perp = 43.82$ MHz. On the other hand, Curl's approximate expression,[49] which for $H_2^+$ may be written

$$d_\perp^{\text{Curl}} = (g_e/\mu R^2)(1 - g_\perp/g_e)\ , \qquad (77)$$

gives the inaccurate result $d_\perp^{\text{Curl}} = 75.56$ MHz when the value of $1 - g_\perp/g_e$ in Table III is used. Looking at this in another way, one can say that Curl's expression, when used with the exact value of $d_\perp$, predicts the result $1 - g_\perp/g_e = 12.21\times10^{-6}$, in serious disagreement with the value $1 - g_\perp/g_e = 21.06\times10^{-6}$ from Table III.

## V. SUMMARY

A theoretical framework has been presented from which precise electronic $g$ values for molecules may be obtained. The theory has been applied to the calculation of $g$ values and related magnetic properties for $H_2^+$, $HD^+$, and $D_2^+$. A comparison of these results, which are expected to be accurate to about 0.1 ppm, with experimental measurements should provide the first precision tests of the theory of molecular $g$ factors.

## ACKNOWLEDGMENT

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## APPENDIX A

Ramsey's expression[25] for the nuclear magnetic shielding tensor is obtained readily within the present formalism. Again one uses Pryce's degenerate perturbation theory[22] with the Hamiltonian of Eq. (39), but with supplemental terms added to $\mathcal{H}^{(1)}$ to describe the interaction of the nuclear spin. The additional terms, one for each nucleus $X$, are

$$\mathcal{H}_X^{(1)} = -g_X\mu_n\vec{I}_X\cdot\vec{B}$$
$$+\frac{e}{m_e}g_X\mu_n\vec{I}_X\cdot\sum_i\frac{\vec{L}_{iX}}{r_{iX}^3}$$
$$+\frac{e^2}{m_e}g_X\mu_n\vec{I}_X\cdot\sum_i\frac{\vec{r}_{iX}\times\vec{A}_{iC}}{r_{iX}^3}\ , \qquad (A1)$$

where $\mu_n = e/2M_p$ is the nuclear magneton and where the symbol $\vec{I}_X$ is used for the spin of nucleus $X$. The first term in the above expression comes from $\mathcal{H}_5$ in Eq. (35), and the remaining two terms both come from the spin-other-orbit term $\mathcal{H}_4$ in Eq. (34). [Note that when the interactions are written in terms of the nuclear magneton $\mu_n$, as in (A1), rather than in terms of $e_X/2m_X$, as in Eqs. (34) and (35), this implies a slightly different definition for the nuclear $g$ values. The definition used in this Appendix is the usual one for nuclei.] These additional terms give rise to an effective nuclear-spin Hamiltonian

$$\mathcal{H}_X^{\text{eff}} = -g_X\mu_n\vec{I}_X\cdot\vec{B}$$
$$+g_X\mu_n\vec{I}_X\cdot\left\{\frac{e^2}{2m_e}\langle\psi_0^{(0)}|\sum_i\frac{\vec{r}_{iC}\cdot\vec{r}_{iX}\overleftrightarrow{1}-\vec{r}_{iC}\vec{r}_{iX}}{r_{iX}^3}|\psi_0^{(0)}\rangle\right.$$
$$\left.+4\left(\frac{e}{2m_e}\right)^2\sum_{n\neq0}\frac{\langle\psi_0^{(0)}|\sum_i r_{iX}^{-3}\vec{L}_{iX}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\sum_i\vec{L}_{iC}|\psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right\}\cdot\vec{B}\ , \qquad (A2)$$

which may be written

$$\mathcal{H}_X^{\text{eff}} \equiv -g_X\mu_n\vec{I}_X\cdot(\vec{1}-\vec{\sigma}_X)\cdot\vec{B}\,. \tag{A3}$$

The quantity inside the curly brackets in (A2) is Ramsey's expression for the nuclear magnetic shielding tensor $\vec{\sigma}_X$ for nucleus $X$. This same quantity appears in the effective electron-spin Hamiltonian given in Eq. (43).

## APPENDIX B

Here Eq. (73) is derived. Expanding Eq. (40) in terms of the internal coordinates gives a term

$$\mathcal{H}_0^1 = -(1/\mu R^2)\,\vec{L}_{eC}\cdot\vec{N}\,. \tag{B1}$$

When Pryce's perturbation method[22] is used this term combines with the spin-orbit coupling term (41b) to give a term in the resulting effective Hamiltonian which is equal to

$$\mathcal{H}_{\text{spin-rot}}^{\text{eff}(2)} = -\frac{(g_e-1)}{\mu R^2}\,\vec{S}\cdot\sum_{X=A,B} Z_X\left\{\frac{e^2}{m_e^2}\sum_{n\neq 0}\frac{\langle\psi_0^{(0)}|r_{eX}^{-3}\,\vec{L}_{eX}|\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\vec{L}_{eC}|\psi_0^{(0)}\rangle}{E_0^{(0)}-E_n^{(0)}}\right\}\cdot\vec{N}\,. \tag{B2}$$

Comparison of the quantity inside the curly brackets of Eq. (B2) with that inside the curly brackets of Eq. (A2) then leads to Eq. (73).

## APPENDIX C

The major emphasis of this paper has been placed upon the precise theory of the *electronic* $g$ tensor for a molecule. However, it should be remembered that the molecular Zeeman effect also includes the interaction of the rotational and nuclear-spin magnetic moments with the external field and that these interactions, although generally about 2000 times smaller than the electronic interaction, must be taken into account when comparing the calculated results of the theory with precise experimental measurements. The theory describing these interactions is well understood to the degree of accuracy required here.[25,48] One simply adds the relevant terms to the effective Hamiltonian of Eq. (71) to obtain

$$\mathcal{H}^{\text{eff}} = g_s\mu_B\vec{S}\cdot\vec{B} - g_R\mu_n\vec{N}\cdot\vec{B} - \sum_X g_X\mu_n\vec{I}\cdot\vec{B} + \mathcal{H}_{\text{aniso}}\,, \tag{C1}$$

where $g_s \equiv g_{\text{av}}$ is the average electronic $g$ factor defined previously, $g_R$ is the rotational $g$ value, $\mathcal{H}_{\text{aniso}}$ represents the last term in Eq. (71), and where the other symbols have their usual meanings. Once the individual $g$ values appearing in Eq. (C1) are known, angular momentum coupling techniques may be used to combine them to form a resultant molecular $g$ value $g_J$ or $g_F$ in the usual ways.[51] For the cases of $H_2^+$, $HD^+$, and $D_2^+$ the nuclear $g$ values are readily available and the rotational $g$ values may be calculated from the relation[48,51]

$$g_R = (M_p/2\mu)\,[1-(8/R^2)\chi_\perp^{(2)}]\,, \tag{C2}$$

where $M_p$ is the proton mass, $\mu$ is the nuclear reduced mass, and $\chi_\perp^{(2)}$ is the second-order part of the diamagnetic susceptibility component perpendicular to the internuclear axis and which is evaluated taking the origin of the electronic orbital angular momentum $\vec{L}$ to be at the midpoint of the internuclear axis. As a first calculation of $g_R$ the value $\chi_\perp^{(2)} = 0.0378$ given in Table II can be used in Eq. (C2); this gives the results $g_R(H_2^+) = 0.9244$, $g_R(HD^+) = 0.6933$, and $g_R(D_2^+) = 0.4622$. Vibrational-rotational corrections to these values, which are expected to be of the order 1% or 2% for the lower vibrational-rotational levels, will be left for a future calculation.

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[1] If the molecule possesses a net electronic orbital angular momentum, there is an additional first-order interaction with the magnetic field; even so, the combined interaction is often written in the form of Eq. (2) and $\vec{S}$ is then called a "fictitious" spin.

[2] R. A. Hegstrom, Phys. Rev. 184, 17 (1969); H. Grotch, Phys. Rev. A 2, 1605 (1970).

[3] H. Grotch and R. A. Hegstrom, Phys. Rev. A 4, 59 (1971); 8, 2771 (1973).

[4] H. Grotch and R. Kashuba, Phys. Rev. A 7, 78 (1973).

[5] R. A. Hegstrom, Phys. Rev. A 7, 451 (1973).

[6] H. Grotch and R. A. Hegstrom, Phys. Rev. A 8, 1166 (1973); P. G. Barkley and R. A. Hegstrom, *ibid.* 14, 1574 (1976).

[7] M. L. Lewis and V. W. Hughes, Phys. Rev. A 11, 383 (1975).

[8] R. A. Hegstrom, Phys. Rev. A 11, 421 (1975).

[9] W. M. Hughes and H. G. Robinson, Phys. Rev. Lett. 23, 1209 (1969).

[10] D. J. Larson, P. A. Valberg, and N. F. Ramsey, Phys. Rev. Lett. 23, 1369 (1969).

[11] F. G. Walther, W. D. Phillips, and D. Kleppner, Phys. Rev. Lett. 28, 1159 (1972).

[12] D. J. Larson and N. F. Ramsey, Phys. Rev. A 9, 1543 (1974).

[13] P. F. Winkler, D. Kleppner, T. Myint, and F. G. Walther, Phys. Rev. A 5, 83 (1972).

[14] J. S. Tiedeman and H. G. Robinson, Phys. Rev. Lett. 39, 602 (1977).

[15] C. E. Johnson and H. G. Robinson, Bull. Am. Phys. Soc. 23, 621 (1978).

[16] E. Aygün, B. D. Zak, and H. A. Shugart, Phys. Rev. Lett. 13, 803 (1973).

[17] G. M. Keiser, H. G. Robinson, and C. E. Johnson, Phys. Rev. Lett. 35, 1223 (1975); Phys. Rev. A 16, 822 (1977).

[18] B. E. Zundell and V. W. Hughes, Phys. Lett. A 59, 381 (1976).

[19] K. D. Böklen, W. Foerster, H. H. Fuchs, G. Nachtsheim, and W. Nitschke, Z. Phys. A 282, 249 (1977).

[20] R. A. Hegstrom, Chem. Phys. Lett. 36, 548 (1975).

[21] H. A. Schuessler and H. G. Dehmelt (private communications).

[22] M. H. L. Pryce, Proc. Phys. Soc. London Sec. A 63, 25 (1950).

[23] A. J. Stone, Proc. R. Soc. London Ser. A 271, 424 (1963).

[24] P. W. Atkins and A. M. Jamieson, Mol. Phys. 14, 425 (1967).

[25] N. F. Ramsey, Phys. Rev. 78, 699 (1950).

[26] G. Hunter and H. O. Pritchard, J. Chem. Phys. 46, 2146 (1967).

[27] Not shown in the Hamiltonian are terms formally of order $\alpha^3\mu_B B$ which arise from the Lamb-shift-type radiative correction combined with retardation corrections to the Breit potential. These terms are apparently nonzero only for molecules with a nonvanishing total electronic orbital angular momentum (see Refs. 3–5).

[28] W. E. Lamb, Jr., Phys. Rev. 85, 259 (1952).

[29] For example, Ref. 5.

[30] C. Lhuillier, Ph.D. thesis (Université de Paris VI, 1976) (unpublished).

[31] R. A. Hegstrom and C. Lhuillier, Phys. Rev. A 15, 1797 (1977).

[32] C. Lhuillier and J. P. Faroux, J. Phys. (Paris) 38, 747 (1977).

[33] If the molecule contains atoms with large electrical charges on nuclei, then it may be necessary to go to higher orders of perturbation theory or to use relativistic wave functions.

[34] D. M. Bishop and R. W. Wetmore, Mol. Phys. 26, 145 (1973).

[35] C. L. Beckel, B. D. Hansen II, and J. M. Peek, J. Chem. Phys. 53, 3681 (1970).

[36] S. T. Epstein, J. Chem. Phys. 65, 5526 (1976).

[37] D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. R. Soc. London Ser. A 246, 215 (1953).

[38] D. G. Anderson, Math. Comput. 19, 477 (1965).

[39] See, for example, Z. Kopal, *Numerical Analysis* (Wiley, New York, 1961).

[40] IBM subroutine DGELS was used. [IBM System/360 Scientific Subroutine Package, (360A-CM-03X) version II].

[41] T. B. Garrett and D. Zeroka, Int. J. Quantum Chem. 6, 651 (1972).

[42] See, for example, J. C. Slater, *Quantum Theory of Molecules and Solids*, Vol. 1 (McGraw-Hill, New York, 1963), Chap. 2.

[43] S. Cohen, J. R. Hiskes, and R. J. Riddell, Jr., Phys. Rev. 119, 1025 (1960).

[44] H. Wind, J. Chem. Phys. 42, 2371 (1965); 43, 2956 (1965).

[45] G. Hunter and H. Pritchard, J. Chem. Phys. 46, 2153 (1967).

[46] G. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables 14, 11 (1974).

[47] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, 1961), Chap. 13.

[48] B. R. Judd, *Angular Momentum Theory for Diatomic Molecules* (Academic, New York, 1975), Chap. 8, p. 174.

[49] R. F. Curl, Jr., Mol. Phys. 9, 585 (1965).

[50] M. Cohen, R. P. McEachran, and I. R. Schlifer, Chem. Phys. Lett. 49, 374 (1977).

[51] W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley-Interscience, New York, 1970), Chap. 11.