

## Vibrational and Centrifugal Effects on the Magnetic Susceptibility and Rotational Magnetic Moment of the Hydrogen Molecule\*

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The effects of nuclear motion on the magnetic susceptibility and rotational magnetic moments of  $H_2$ , HD, and  $D_2$  are considered. The magnetic susceptibility and the rotational magnetic moment have been evaluated as a function of the internuclear distance by a variational procedure using the accurate wave functions of Kolos and Roothaan. A careful vibrational averaging has been performed to obtain these magnetic properties for  $H_2$ , HD, and  $D_2$  in a number of vibrational-rotational states. A critical test of these calculations is provided by a comparison of the calculated  $\langle\mu_R^e\rangle_{v,j}$ 's (electronic contribution to the rotational magnetic moment) with experiment. While our one-parameter variational calculations only account for 70% of the experimental  $\langle\mu_R^e\rangle_{v,j}$ 's, ratios of the calculated  $\langle\mu_R^e\rangle_{v,j}$ 's between the three isotopic molecules in their respective vibrational-rotational states are in remarkable agreement with the experimental ratios (within 0.3%). A similar vibrational averaging of  $\mu_R^e(R)$  obtained by Espe using a four-parameter variational calculation based upon the zero-order wave function of Newell indicates that while the theoretical  $\langle\mu_R^e\rangle_{v,j}$ 's are now within 10% of the experimental values, the ratios of the  $\langle\mu_R^e\rangle_{v,j}$ 's are not in as good agreement with experiment. The implication of these results on the molecular-beam method of obtaining molecular dipole moments from isotopic variations of the rotational magnetic moment is discussed.

### INTRODUCTION

MOTION of the nuclear framework, namely vibrational motion and centrifugal stretching of molecules, can have significant effects on electric and magnetic properties of molecules. The influence of zero-point vibration on the nuclear quadrupole interaction in molecules has received early attention and has been investigated quite extensively.<sup>1,2</sup> More recently, the effects of nuclear motion on magnetic properties as well as other electrical properties have also been considered. Notable contributions have been made by Newell,<sup>3</sup> Ramsey,<sup>4-6</sup> Ishiguro,<sup>7-9</sup> Marshall,<sup>10</sup> and Auffray.<sup>11</sup>

For a few molecules, it is possible to make *ab initio* calculations of an electric or magnetic property as a function of the nuclear coordinates. In these instances, the effects of the nuclear motion are generally taken into consideration by performing the appropriate vibrational average. More frequently, however, such vibrational averages are not readily evaluated due to lack of knowledge of the dependence of the property concerned on the molecular geometry. For such situations, Ramsey has assumed, in the case of a diatomic molecule, that the

property of interest can be expressed as  $F_e(R/R_e)^n$ , where  $F_e$  is the value of the property at the equilibrium internuclear distance and  $R/R_e$  the ratio of the instantaneous internuclear distance to its equilibrium value.<sup>5</sup> An assumption of this type was first introduced by Newell<sup>3</sup> in his vibrational averaging of the high-frequency part of the magnetic shielding constant in  $H_2$ . Ramsey has extended this assumption to the high-frequency part of the magnetic susceptibility and to the electronic parts of the spin-rotational constant and the rotational magnetic moment.

The theory of Ramsey is particularly adaptable to the interpretation of experimental results from molecular-beam experiments.<sup>6</sup> Thus, Ramsey and his co-workers have empirically determined  $n$  for the electronic contribution to the rotational magnetic moment as well as the high-frequency part of the magnetic susceptibility in  $H_2$  from precise molecular-beam measurements of the rotational moments of  $H_2$ , HD, and  $D_2$ . Consistent results appeared to be obtained both from the variations of the rotational moment with rotational quantum number and isotopic mass.

While these consistencies perhaps lend support to Ramsey's simplifying assumption, its usefulness has merely been demonstrated in a single case and its general applicability may be questionable. This point has recently been raised in an article by Russell<sup>12</sup> concerning the determination of electric dipole moments of some molecules from changes in the rotational moment upon isotopic substitution. As indicated by Russell, the calculated dipole moment can be affected appreciably if one neglects the effects of vibrational motion on the rotational moment. In the case of LiF, Russell showed that

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<sup>1</sup> A. Nordsieck, Phys. Rev. **58**, 310 (1940).

<sup>2</sup> G. F. Newell, Phys. Rev. **78**, 711 (1950).

<sup>3</sup> G. F. Newell, Phys. Rev. **80**, 476 (1950).

<sup>4</sup> N. F. Ramsey, Phys. Rev. **85**, 937 (1952).

<sup>5</sup> N. F. Ramsey, Phys. Rev. **87**, 1075 (1952).

<sup>6</sup> R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. **94**, 893 (1954); W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, *ibid.* **112**, 1929 (1958).

<sup>7</sup> E. Ishiguro, T. Arai, M. Mizushima, and M. Kotani, Proc. Phys. Soc. (London) **A65**, 178 (1952).

<sup>8</sup> E. Ishiguro, Phys. Rev. **111**, 203 (1958).

<sup>9</sup> E. Ishiguro and S. Koida, Phys. Rev. **94**, 350 (1954).

<sup>10</sup> T. W. Marshall, Mol. Phys. **4**, 61 (1961).

<sup>11</sup> J. P. Auffray, Phys. Rev. **126**, 146 (1962).

<sup>12</sup> A. Russell, J. Chem. Phys. **37**, 214 (1962).

when Ramsey's assumption was employed, an abnormally high value of  $n$  had to be used. While there exists in this case the possibility that the equilibrium internuclear distance may not be accurately determined, it is also likely that Ramsey's assumption is invalid.

It is the purpose of the present paper to show that one can obtain a fair estimate of vibrational effects and their variation with isotopic substitution from *ab initio* calculations. Such a calculation will obviate the simplifying assumptions proposed by Ramsey. In those cases where  $n$  has been determined empirically within the framework of Ramsey's theory, the results will also serve to check the depicted variation of the magnetic property with internuclear distance. Quite often differences in the zero-point motions between isotopic species and centrifugal stretching effects are too small to produce an observable change in the magnetic property under study, in which case a calculation from first principles represents the only way to estimate these vibrational effects.

For this investigation, the molecules  $H_2$ , HD, and  $D_2$  have been chosen for several reasons. First, accurate ground-state wave functions are now available for the hydrogen molecule over a wide range of internuclear distances. Among these are Kolos and Roothaan's single-configuration-28-term function<sup>13</sup> and Fraga and Ransil's LACO-MO function with configuration interaction.<sup>14</sup> Secondly, as mentioned earlier, precise molecular-beam data exist for these molecules in a number of vibration-rotational states. Finally, these molecules do not possess electric dipole moments so that the electronic contribution to the rotational magnetic moment may be calculated directly from an appropriate average of the high-frequency part of the magnetic susceptibility. A comparison of the calculated rotational magnetic moment with experiment then serves as an indication of the accuracy of *ab initio* calculations of the vibrational effects and permits an evaluation of their utility in the determination of dipole moments of heteronuclear diatomic molecules from molecular-beam studies of rotational magnetic moments.

In this work, we are primarily concerned with evaluating the rotational magnetic moment of  $H_2$  as a function of the internuclear distance. In this connection, we need only worry about the electronic contribution since the nuclear contribution is independent of the internuclear separation. Ramsey<sup>5</sup> has shown that the electronic contribution to the rotational moment  $\mu_R^e$ , is related to  $\chi^p(R)/R^2$ , where  $\chi^p$  is the high-frequency part of the magnetic susceptibility. Thus, our problem reduces to the evaluation of  $\chi^p$  as a function of the internuclear distance. Conventional second-order perturbation theory cannot be used here since  $\chi^p$  entails a knowledge of excited-state wave functions and energies, and these are, in general, not known even at the equilibrium inter-

nuclear separation. On the other hand, variational methods have proved to be much more successful<sup>15,16</sup> since they require only a knowledge of the ground-state wave function and a convenient choice of the variational function to represent the perturbed molecule. In fact, Espe<sup>17</sup> has already undertaken a four-parameter variational calculation for the electronic contribution to the rotational magnetic moment in  $H_2$  using Newell's ground-state function.<sup>2</sup> However, Espe considered only three internuclear distances ( $1.3a_0$ ,  $1.4a_0$ , and  $1.5a_0$ ) and it is felt that more points are desirable for a reliable vibrational averaging. More important, we question the accuracy of the Newell function, and felt that it is worthwhile to try out a set of wave functions which have been proven to be more accurate over a wide range of internuclear distances. For these reasons, we have undertaken a variational calculation for  $\chi^p$  using the wave functions of Kolos and Roothaan.<sup>13</sup>

In our present calculations, the diamagnetic part of the susceptibility will also be evaluated using the wave functions of Kolos and Roothaan. An explicit vibrational averaging of this ground-state term in the susceptibility has already been reported by Auffray.<sup>11</sup> These calculations are repeated here as our method of vibrational averaging is different from Auffray's and we employ an *empirical* potential function rather than a *theoretical* one.

For the motional averaging, two different empirical expressions for the vibrational potential will be considered. The calculations will also be performed both with and without the consideration of centrifugal effects and for a number of rotational states. The computer program that we have for the motional averaging is quite general and can be used for a potential function expressed in any functional form. This feature will allow us to perform vibrational calculations for molecules where the Morse potential does not provide an adequate description of the potential surface. Such is the case for the alkali halides<sup>18</sup> and hydrides,<sup>19,20</sup> e.g., LiF and LiH. Our computer program can also be readily modified to include more than one vibrational degree of freedom. This flexibility is desirable since magnetic properties are currently being measured for more complicated molecules. Furthermore, while one might expect stretching vibrations to perturb the electronic system significantly, other modes, in particular bending ones, are more easily excited and their effects are therefore more readily observed. For these vibrations, because of their larger vibrational amplitudes and their larger anharmonicities, the simple harmonic oscillator or the Morse potential is surely inadequate.

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<sup>16</sup> M. Karplus and H. J. Kolker, J. Chem. Phys. **38**, 1263 (1963).

<sup>17</sup> I. Espe, Phys. Rev. **103**, 1254 (1956).

<sup>18</sup> E. Rittner, J. Chem. Phys. **19**, 1030 (1951).

<sup>19</sup> W. A. Klemperer and J. L. Margrave, J. Chem. Phys. **20**, 527 (1952).

<sup>13</sup> W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 231 (1960).

<sup>14</sup> S. Fraga and B. I. Ransil, J. Chem. Phys. **35**, 1967 (1961).

<sup>20</sup> Y. P. Varshni and R. C. Shukla, Rev. Mod. Phys. **35**, 130 (1963).

## I. GENERAL PROCEDURE

Before we can perform the appropriate averaging of a molecular property over the nuclear motion, we must first know the property as a function of the nuclear coordinates. This implies, of course, that the electronic wave functions be known for many nuclear configurations. In performing the vibrational averaging, it is assumed that the Born-Oppenheimer approximation is valid. That is,

$$\psi_{\text{total}} = \psi_e(R)\psi_v\psi_R, \quad (1)$$

where  $\psi_e(R)$  is the electronic wave function for a nuclear configuration described by  $R$ . The average of a molecular property  $\mathbf{O}$  which depends both on the electronic and nuclear coordinates is then given by

$$\begin{aligned} \langle O(R) \rangle &= \int \psi_e^*(R)\psi_v^*\psi_R^*\mathbf{O}\psi_e(R)\psi_v\psi_R d\tau_R d\tau_e \\ &= \int \psi_v^*\psi_R^*\mathbf{O}(R)\psi_v\psi_R d\tau_R, \end{aligned} \quad (2)$$

where

$$\mathbf{O}(R) = \int \psi_e^*(R)\mathbf{O}\psi_e(R) d\tau_e.$$

$d\tau_e$  is the volume element over electronic coordinates and  $d\tau_R$  over nuclear coordinates.

Let us assume that  $O(R)$  has already been determined. We then have to consider how to perform the averaging over the nuclear wave function. Let us illustrate for a diatomic molecule where there is only one mode of vibration. For a given potential function the eigenvalues and eigenfunctions of the Hamiltonian for this nuclear motion can be obtained by variational methods. A convenient variational function would be to expand each nuclear eigenfunction  $\psi_v$  as a linear combination of a complete orthonormal set of functions. The combination coefficients can be obtained from solution of the secular equations. When the potential is expressed as a Taylor's expansion, convenient complete sets to use are the harmonic oscillator<sup>21</sup> or quartic oscillator eigenfunctions,<sup>22</sup> for which the matrix elements of  $x^n$  or  $(R - R_e)^n$  are known. In practice, one chooses a basis set for which the matrix elements of the Hamiltonian are conveniently obtained. Of course, the rapidity of convergence also dictates the choice of the basis set. Once the eigenfunctions for the actual nuclear Hamiltonian are known as linear combinations of basis functions, one can easily obtain the expectation values of  $x^n$  over the nuclear functions. This then permits the evaluation of  $\langle O(R) \rangle$  since  $O(R)$  can be expanded in a Taylor's series in terms of the displacement coordinate. Thus,

$$\langle O(R) \rangle = O(R_e) + \sum_{n=1} \left( \frac{\partial^n O}{\partial R^n} \right)_{R_e} \langle (R - R_e)^n \rangle / n!. \quad (3)$$

<sup>21</sup> E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill Book Company, Inc., New York, 1955), p. 290.

<sup>22</sup> S. I. Chan and D. Stelman, *J. Mol. Spectry*, **10**, 278 (1963).

Extension of the above approach to a triatomic molecule is relatively straightforward. Here normal coordinates will be employed. If the vibrational Hamiltonian is separable in normal coordinates, each normal mode can be treated independently. If interactions between normal modes are significant, these interaction terms can be included as a perturbation to the zeroth-order problem. The vibrational wave function to be employed for the averaging would then be the zeroth-order wave function constructed of product functions from each mode plus correction terms arising from the mixing of modes. Only first-order mixing of normal modes is usually more than adequate in practice. The vibrational averaging is analogous; thus, for a bent triatomic molecule,

$$\begin{aligned} \langle O(Q_1, Q_2, Q_3) \rangle &= O(0, 0, 0) + \sum_{k=1}^3 \left( \frac{\partial O}{\partial Q_k} \right)_{0,0} \langle Q_k \rangle \\ &+ \frac{1}{2} \sum_{j=1}^3 \sum_{k=1}^3 \left( \frac{\partial^2 O}{\partial Q_j \partial Q_k} \right)_{0,0} \langle Q_j Q_k \rangle + \dots, \end{aligned} \quad (4)$$

where  $j, k$  refer to the  $j$ th and  $k$ th normal modes.

The above techniques are of course well known to the molecular spectroscopist, and probably not unfamiliar to those engaged in the calculations of magnetic properties. Except for the method of obtaining the vibrational wave function, our present approach is actually quite similar to Newell's calculations<sup>2</sup> on the quadrupole coupling constant of HD, Ishiguro's calculations<sup>7</sup> on the electric polarizability of H<sub>2</sub>, HD, and D<sub>2</sub>, Ishiguro's calculations<sup>8</sup> on the electron-coupled spin-spin constant in HD, Ishiguro's calculations<sup>9</sup> on the rotational magnetic moment, and Marshall's calculations<sup>10</sup> on the nuclear magnetic shielding constant of H<sub>2</sub>. However, in this work, in order to ensure convergence, the series expansion given by (3) has been taken up to the  $x^6$  term instead of the first two or three terms employed by other research workers.

## II. VIBRATIONAL WAVE FUNCTIONS FOR THE HYDROGEN MOLECULE

A number of empirical potential functions are available for H<sub>2</sub>, most notably the Morse potential,<sup>23</sup> the Dunham potential,<sup>24,25</sup> the Lippincott potential,<sup>26</sup> and the Hulburt-Hirschfelder function.<sup>27</sup> While these are not exact representations of the actual potential surface, they are quite adequate for our purposes, as is evident when these potentials are compared at small vibrational amplitudes ( $< 0.5A$ ) with the "true" potential obtained using the Rydberg-Klein-Rees

<sup>23</sup> P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

<sup>24</sup> J. L. Dunham, *Phys. Rev.* **41**, 713, 721 (1932).

<sup>25</sup> B. P. Stoicheff, *Can. J. Phys.* **35**, 730 (1957).

<sup>26</sup> E. R. Lippincott, *J. Chem. Phys.* **21**, 2070 (1953); E. R. Lippincott and R. Schroeder, *ibid.* **23**, 1131 (1955); D. Steele and E. R. Lippincott, *ibid.* **35**, 1065 (1961).

<sup>27</sup> H. M. Hulburt and J. O. Hirschfelder, *J. Chem. Phys.* **9**, 61 (1941).

method.<sup>28</sup> Of the above empirical potentials, the Morse and Dunham functions are particularly convenient for our present interests. In this work, calculations have been performed for both potential functions.

The Morse potential can be expanded in a Taylor series about the equilibrium internuclear distance. The Dunham potential is already in the above form. In either case, the vibrational Hamiltonian is given by

$$\mathcal{H} = \frac{p^2}{2\mu} + \sum_{n=2}^{\infty} a_n x^n. \quad (5)$$

In this work, we have truncated the potential energy after the  $x^6$  term. Errors due to this truncation will be discussed later.

The following transformation,<sup>22</sup>

$$\begin{aligned} X &= (8\mu a_2/\hbar^2)^{1/4} x, \\ P &= (2/\mu a_2 \hbar^2)^{1/4} p, \end{aligned} \quad (6)$$

reduces the computation to dimensionless variables. Thus,

$$\mathcal{H} = \frac{\hbar}{4} \left( \frac{2a_2}{\mu} \right)^{1/2} \left\{ P^2 + X^2 + \sum_{n=3} a_n \left( \frac{\mu}{2a_2} \right)^{1/2} \left( \frac{\hbar^2}{8\mu a_2} \right)^{n/4} X^n \right\}. \quad (7)$$

For  $H_2$  the Morse/Dunham function can be shown to reduce to

$$\mathcal{H} = (1100.1 \text{ cm}^{-1}) \left\{ P^2 + X^2 - \frac{0.16951}{0.18789} X^3 + \frac{0.016761}{0.025826} X^4 - \frac{0.0012176}{0.003368} X^5 + \frac{0.000071094}{0.00043220} X^6 \right\}. \quad (8)$$

Analogous expressions hold for HD and  $D_2$ . Since  $X^n$  are reduced variables independent of  $\mu$  and potential constants, one set of matrix elements are applicable to all the isotopes. For different isotopes, we have merely different constants to work with.

The above transformation has facilitated calculations in the harmonic-oscillator representation, since  $P^2 + X^2$  is diagonal in this representation. The anharmonicity of the potential well in our case is such that reasonable convergence in the computations may be obtained by treating the oscillator as a slightly perturbed harmonic oscillator. For larger anharmonicities, the quartic representation may be conveniently employed.<sup>22,29</sup>

We have so far restricted our discussion to the vibrational motion alone. However, for a rotating diatomic molecule, the vibrational Hamiltonian should be modified to include the effects of the centrifugal potential. This effect is easily taken into consideration as

$\hbar^2(J)(J+1)/2\mu R^2$  can be expanded about the equilibrium distance  $R_e$ . Terms containing  $(R-R_e)^n$  can be added to the vibrational potential to yield an effective potential for the nuclear motion.

The following results have been obtained with the Hamiltonian matrix set up in the harmonic-oscillator representation. Twenty basis functions were employed. That is,

$$\psi_v = \sum_{n=0}^{19} T_{nv} \phi_n^{\text{HO}}. \quad (9)$$

Diagonalization was carried out on an IBM-7090 computer. A check on convergence was provided by the magnitude of the coefficient  $T_{19,v}$ . For  $v=0, 1$ , and  $2$ ,  $T_{19,v} \approx 10^{-7} - 10^{-6}$ .

The expectation values of  $x^n$  in the diagonal representation are easily obtained from a similarity transformation. Thus,

$$\langle x^n \rangle = \mathbf{T}^{-1} \mathbf{x}^n \mathbf{T}. \quad (10)$$

These expectation values are extremely sensitive to the accuracy of the wave function. This is particularly the case with expectation values of odd powers of  $x$ , since in the harmonic-oscillator representation, these expectation values are by symmetry equal to zero and a small asymmetry in the potential well will make these  $\langle x^n \rangle$  nonzero. This slight asymmetry may cause a similar absolute change in the expectation values of even powers of  $x$ . However, since these are already finite in the original representation, the percentage correction is an order of magnitude smaller. Thus, matrix elements of even powers of  $x$  are relatively insensitive to the accuracy of the wave function compared to those involving odd powers of  $x$ . By the same token, since wave functions are determined by the nature of the potential well, these expectation values are extremely sensitive to the potential well. For instance, truncation of Morse potential expansion beyond the cubic term can be shown<sup>10</sup> to give a  $\langle x \rangle_{0,0}$  which is 30% too low. The mean-square displacement is about 10% off in the same calculation.

In Table I, we have tabulated the expectation values of  $x, x^2, x^3, x^4, x^5$ , and  $x^6$  for  $H_2$ , HD, and  $D_2$ . Results are given for a number of vibrational and rotational states. Only the values obtained employing the Morse function are presented. Corresponding expectation values for the Dunham potential appear to be less reliable judging from the accuracy with which the first few energy levels are reproduced by this potential function. In general, the two sets of expectation values differed in the second or third figure depending upon whether the operator  $x^n$  is odd or even.

In Table II, the first few energy levels determined from the two potential functions presently under study are compared with experiment. It is clear that the Dunham potential is less satisfactory than the Morse function if the energy is used as a criterion for the applicability of the potential function.

<sup>28</sup> J. T. Vandarslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, *J. Mol. Spectry*, **3**, 17 (1959).

<sup>29</sup> S. I. Chan, D. Stelman, and L. E. Thompson (unpublished).

TABLE I. Expectation values of powers of the vibrational displacement for H<sub>2</sub>, HD, and D<sub>2</sub>.<sup>a</sup>

	$\langle(R-R_e)\rangle$ $\times 10^1$	$\langle(R-R_e)^2\rangle$ $\times 10^1$	$\langle(R-R_e)^3\rangle$ $\times 10^2$	$\langle(R-R_e)^4\rangle$ $\times 10^2$	$\langle(R-R_e)^5\rangle$ $\times 10^3$	$\langle(R-R_e)^6\rangle$ $\times 10^3$
H <sub>2</sub>						
$v=0$ $J=0$	0.42735	0.30196	0.45382	0.29158	0.80012	0.50013
1	0.44964	0.30421	0.47469	0.29630	0.83489	0.51256
2	0.49402	0.30899	0.51679	0.30628	0.90596	0.53881
$v=1$ $J=0$	1.3178	1.0410	3.2441	2.0437	9.3099	5.9040
HD						
$v=0$ $J=0$	0.36924	0.25793	0.33678	0.21124	0.50816	0.30562
1	0.38588	0.25938	0.35004	0.21385	0.52685	0.31150
D <sub>2</sub>						
$v=0$ $J=0$	0.30064	0.20716	0.22169	0.13505	0.26923	0.15436
1	0.31168	0.20794	0.22872	0.13618	0.27707	0.15641

<sup>a</sup> Results are for the Morse potential and are given in atomic units.

As a check on possible errors which may arrive from truncation of the series in expression (5), the energy levels calculated from the truncated Morse potential are also compared with the results of an exact calculation.<sup>23</sup> It is seen (Table II) that for the two lowest vibrational states, these errors are within the margins of discrepancy between the experimental and calculated values. A few of our calculated expectation values can also be compared with those from an exact calculation as Ishiguro and co-workers<sup>7</sup> have obtained closed form expressions for the matrix elements of  $x$ ,  $x^2$ , and  $x^3$  for the ground vibrational state of the Morse oscillator. A comparison of our calculated values with those reported by these investigators for H<sub>2</sub>, HD, and D<sub>2</sub> in their respective ground vibrational-rotational states reveals good agreement. Discrepancies, which are in the fourth significant figure, are most likely due to our truncation of the expanded Morse potential, but may also be due to slightly different potential constants employed in the two computations.

TABLE II. A comparison between the calculated and experimental vibrational energy levels of H<sub>2</sub>.

	Morse		Dunham cm <sup>-1</sup>	Experiment <sup>a</sup> cm <sup>-1</sup>
	Exact cm <sup>-1</sup>	Truncated cm <sup>-1</sup>		
$v=0$	2168.6	2168.8	2180.9	2170.08
$v=1$	6316.1	6319.5	6378.2	6331.20
$v=2$	10 210.7	10 234.5	10 492.7	10 257.15

<sup>a</sup> See Ref. 22 of text.

### III. CALCULATIONS OF THE SUSCEPTIBILITY AND THE ROTATIONAL MOMENT AS A FUNCTION OF INTERNUCLEAR DISTANCE

We next consider the calculation of the susceptibility and the rotational magnetic moment of the hydrogen molecule as a function of internuclear distance. Kolos and Roothaan have already obtained  $\langle r_e^2 \rangle$  and  $\langle 3z_e^2 - r_e^2 \rangle$  as a function of the internuclear distance using their single-configuration-28-term function. These expectation values are needed in the diamagnetic susceptibility and

in the variational calculation of the paramagnetic susceptibility and the rotational moment.  $r_e$  and  $z_e$  denote the electronic coordinates measured from the electronic centroid.

#### a. Susceptibility

With the electronic centroid as the origin of the magnetic vector potential,

$$\begin{aligned} \chi_{11}^d &= \chi_{xx}^d = \chi_{yy}^d = -\frac{1}{2}\alpha^2 a_0^3 \langle y_e^2 + z_e^2 \rangle, \\ \chi_{11}^d &= \chi_{zz}^d = -\frac{1}{2}\alpha^2 a_0^3 \langle x_e^2 + y_e^2 \rangle. \end{aligned} \quad (11)$$

$\langle x_e^2 \rangle$ ,  $\langle y_e^2 \rangle$ , and  $\langle z_e^2 \rangle$  are readily computed from the tables of  $\langle r_e^2 \rangle$  and  $\langle 3z_e^2 - r_e^2 \rangle$  reported by Kolos and Roothaan.

The paramagnetic susceptibility,

$$\chi_{11}^p = \chi_{xx}^p = \chi_{yy}^p, \quad (12)$$

cannot be rigorously calculated from the ground-state wave function. However, using a variational procedure proposed earlier,<sup>15</sup> an approximate expression may be obtained in terms of known expectation values over the ground-state function. If

$$\psi_e = (1 + \mathbf{H} \cdot \mathbf{P}(H)) \psi_e^0, \quad (13)$$

and the perturbation  $\mathbf{P}(H)$  is chosen to be

$$\begin{aligned} P_x(H) &= aiy_e z_e, \\ P_y(H) &= aix_e z_e, \\ P_z(H) &= 0, \end{aligned} \quad (14)$$

where  $a$  is the variation parameter,

$$\chi_{xx}^p \cong \frac{1}{2}\alpha^2 a_0^3 \langle (z_e^2 - x_e^2)^2 / (z_e^2 + x_e^2) \rangle. \quad (15)$$

By symmetry,

$$\chi_{11}^p = \chi_{zz}^p = 0. \quad (16)$$

The use of a single variational parameter in the perturbation function  $\mathbf{P}(H)$  may cause some concern. Karplus and Kolker<sup>16</sup> have recently made similar computations using 1-4 variational parameters and using the wave function of Fraga and Ransil. Their calculations

were undertaken with the origin of the magnetic vector potential at one of the protons. In order to compare their results with ours, a translation of the origin has been made in the usual manner.<sup>30</sup> It was found that this change in gauge accounted for more than 90% of their reported<sup>31</sup>  $\chi_{1^p}[H]$ . Recently, it has been pointed out that the paramagnetic susceptibility is a minimum when the origin of the vector potential is chosen at the center of the electronic charge distribution.<sup>30</sup> As a translation of the origin is easily made without a knowledge of  $\psi_0$  or the perturbation function  $\mathbf{P}$ , calculations undertaken at the centroid of electronic charges provide a better absolute check on the convergence of the variation procedure. In Table III, Karplus' results and our present

TABLE III. The high-frequency part of the magnetic susceptibility of  $\text{H}_2$ ,  $R = R_e = 1.40a_0$  (in units of  $\frac{1}{2}\alpha^2 a_0^3$ ).

		$\chi_{1^p}[H]$	$\chi_{1^p}[C]$
Karplus <sup>a</sup>	1 parameter	0.4914	0.0010
	2 parameters	0.5264	0.0360
	3 parameters	0.5267	0.0363
	4 parameters	0.5322	0.0418
Espe <sup>b</sup>	1 parameter		0.04222
	2 parameters		0.04536
	3 parameters		0.04674
	4 parameters		0.04756
Present work			0.0374
Experimental <sup>c</sup>		0.5435	0.0531

<sup>a</sup> M. Karplus and H. J. Kolker, *J. Chem. Phys.* **38**, 1263 (1963).

<sup>b</sup> I. Espe, *Phys. Rev.* **103**, 1254 (1956).

<sup>c</sup> Computed from Ramsey's rotational moment data [R. G. Barnes, P. J. Bray, and N. F. Ramsey, *Phys. Rev.* **94**, 893 (1954)] assuming that  $(\chi_{1^p}(R)/R^2) = [\chi_{1^p}(R_e)/R_e^2](R/R_e)^n$ .

values for the equilibrium internuclear separation are listed for comparison. It is seen that while Karplus' four-term variation function has accounted for 98% of the experimental  $\chi_{1^p}[H]$ , it only accounted for 79% of  $\chi_{1^p}[C]$ . Our single-parameter variational calculation can be seen to be an improvement over Karplus' three-parameter calculation. Since the perturbation function  $axz_c = axz + a(R/2)z \simeq axz + bz$ , Karplus' two-parameter variational function is essentially equivalent to our one-parameter function and our better value here may be attributed to a more accurate  $\psi_e^0$  employed in this present work.

Improvement on our present value of  $\chi_{1^p}[C]$  may be obtained presumably with more parameters in our perturbation function. However, the work of Karplus seems to indicate that experimental agreement cannot be attained with less than three parameters. Espe<sup>17</sup> has shown that one can get about 10% increase in  $\chi_{1^p}[C]$  by using a four-parameter instead of a one-parameter variational function (see Table III). However, even with this improvement, the calculated value

would still be  $\sim 20\%$  off from the experimental value. The fact that Espe's four-parameter calculation is only 10% off from the experimental value should perhaps not be taken too seriously since his one-parameter calculation is already quite good. In fact, it is better than Karplus' four-parameter calculation. This better agreement is, however, probably accidental, since Newell's zero-order function yields a smaller binding energy than both Fraga and Ransil's function and Kolos and Roothaan's function. In the light of these considerations, and in view of the fact that the aim of the present work is not a study of the accuracy and convergence of the variational procedure with regard to the calculation of magnetic properties of molecules, but rather an understanding of vibrational effects and their consequences, we have not attempted to improve on our one-parameter calculation.

In the above manner, we have evaluated  $\chi_{1^d}$ ,  $\chi_{11^d}$ , and  $\chi_{1^p}$  for internuclear distances of  $1.00a_0$ ,  $1.10a_0$ ,  $1.20a_0$ ,  $1.30a_0$ ,  $1.35a_0$ ,  $1.40a_0$ ,  $1.45a_0$ ,  $1.50a_0$ ,  $1.60a_0$ ,  $1.70a_0$ , and  $1.80a_0$ . The method of least squares has been employed to obtain a power-series expansion of these quantities about the equilibrium distance.

$$\chi_{xx^p}(R) = \chi_{xx^p}(R_e) + b_1x + b_2x^2 + \dots + b_6x^6 + \dots \quad (17)$$

## b. Rotational Moment

For a linear  $^1\Sigma$  molecule, the rotational moment  $\mu_R$ , or the rotational  $g$  value  $g_J$ , can be obtained from  $\chi_{1^p}$  as follows<sup>32</sup>:

$$g_J = \frac{\mu_R}{J\mu_N} = M \left\{ \frac{1}{I} \sum_N \xi_N R_N^2 + \left( \sum_N \xi_N \right) \frac{D^2 - d^2}{I} - \frac{4mc^2 \chi_{1^p}}{e^2 I} \right\}. \quad (18)$$

Here  $M$  is proton mass,  $I$  is the moment of inertia about the center of mass,  $\xi_N$  is the charge of the  $N$ th nucleus, and  $R_N$  is the distance of the  $N$ th nucleus from the nuclear centroid.  $D$  and  $d$  denote respectively the distances of the nuclear centroid and electronic centroid relative to the center of mass.

For  $\text{H}_2$  and  $\text{D}_2$ , the second term in Eq. (18) vanishes and the above expression reduces to

$$g_J = \frac{\mu_R}{J\mu_N} = \frac{1}{2\mu'} \frac{4mc^2 \chi_{1^p}}{e^2 \mu' R^2}. \quad (19)$$

$\mu'$  is the reduced mass of the molecule in proton mass units.

For HD, Eq. (19) is also applicable within the Born-Oppenheimer approximation. However, when higher order corrections are taken into consideration, the nuclear and electronic centroids of HD will not vanish.

<sup>30</sup> S. I. Chan and T. P. Das, *J. Chem. Phys.* **37**, 1527 (1962).

<sup>31</sup> [ ] denotes origin of vector potential: [H] for proton, and [C] for electronic centroid.

<sup>32</sup> N. F. Ramsey, *Molecular Beams* (Oxford University Press, New York, 1956), p. 170.

TABLE IV. The magnetic susceptibility of H<sub>2</sub>, HD, and D<sub>2</sub> (in units of  $\frac{1}{2}\alpha^2 a_0^3$ ).

		$\chi_1^d$	$\chi_{11}^d$	$\chi_1^p$	$\chi$	$\chi_{11} - \chi_1$
H <sub>2</sub>	Present work					
	$R_e$	-1.7819	-1.5238	0.03739	-1.6709	0.2207
	$v=0$ $J=0$	-1.8298	-1.5453	0.04573	-1.7045	
	$J=1$	-1.8321	-1.5465	0.04601	-1.7062	0.2396
	$J=2$	-1.8366	-1.5489	0.04656	-1.7097	
	$v=1$ $J=0$	-1.9333	-1.5874	0.06641	-1.7737	
	Auffray <sup>a</sup>					
	$v=0$ $J=1$	-1.837±0.002	-1.550±0.002	0.0654±0.0006	-1.698±0.002	0.223±0.001
	Espe <sup>f</sup>					
	$R_e$			0.04756		
$v=0$ $J=1$			0.06259			
Experiment						
$R_e$			0.0531 <sup>g</sup>			
$v=0$ $J=1$			0.0654±0.0003 <sup>b</sup>	-1.685±0.0007 <sup>d</sup>	0.232±0.013	
$J=2$			0.0662±0.0005 <sup>b</sup>			
HD	Present work					
	$v=0$ $J=0$	-1.8232	-1.5424	0.04450	-1.6999	
	$J=1$	-1.8249	-1.5433	0.04470	-1.7012	0.237
	Experiment					
$v=0$ $J=1$			0.0637±0.0002 <sup>e</sup>		0.226±0.013 <sup>e</sup>	
D <sub>2</sub>	Present work					
	$v=0$ $J=0$	-1.8155	-1.5390	0.04308	-1.6946	
	$J=1$	-1.8166	-1.5397	0.04321	-1.6955	0.234
	Experiment					
$v=0$ $J=1$			0.0617±0.0002 <sup>b</sup>		0.222±0.025 <sup>b</sup>	

<sup>a</sup> J. P. Auffray, Phys. Rev. **126**, 146 (1962).

<sup>b</sup> R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. **94**, 1893 (1954).

<sup>c</sup> W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, Phys. Rev. **112**, 1929 (1958).

<sup>d</sup> G. G. Havens, Phys. Rev. **43**, 992 (1933). Note that the experimental susceptibility is a weighted average over several rotational states.

<sup>e</sup> See footnote c, Table III.

<sup>f</sup> I. Espe, Phys. Rev. **103**, 1254 (1956).

We have estimated the order of magnitude of this term using the dipole moment function calculated by Blinder<sup>38</sup> and have found its contribution to the HD rotational moment to be negligible in importance.

The nuclear contribution to the rotational moment of a diatomic molecule is independent of the internuclear distance. Thus, the variation of rotational moment with vibrational-rotational state and isotopic mass can be completely attributed to the effects of the nuclear motion on the electronic contribution  $\chi_1^p/R^2$ . In Fig. 1, our calculated  $\chi_1^p(R)/R^2$  is plotted versus the internuclear distance  $R$  on a semilogarithmic plot. For comparison, the "experimental" variation of this quantity with internuclear distance as determined by Ramsey's molecular-beam studies<sup>6</sup> is shown. The latter is a plot of the function  $\chi_1^p(R)/R^2 = [\chi_1^p(R_e)/R_e^2](R/R_e)^n$ , where  $n$  has been determined from the variations of the rotational moment with rotational quantum number and isotopic mass. The depicted agreement in the shapes of the theoretical and experimental curves is striking indeed. Since our one-parameter calculation of  $\chi_1^p(R_e)$  is only 70% of the experimental value, the  $R$  dependence of these curves is best compared and examined by translating the calculated curve until it coincides with the experimental curve at the equilibrium distance.

<sup>38</sup> S. Blinder, J. Chem. Phys. **32**, 105 (1960).

In Fig. 1, we have also plotted the three points from Espe's four-parameter calculation at  $R=1.30, 1.40,$  and  $1.50a_0$ . These results seem to fit the experimental variation between 1.40 and  $1.50a_0$  quite well. However, the variation of  $\chi_1^p(R)/R^2$  between 1.30 and  $1.40a_0$  is quite different. The origin of this discrepancy is not clear; whether it is due to an error in Espe's variational calculation or a property of Newell's ground-state function cannot be resolved without repeating Espe's calculation at  $1.30a_0$  or at some other internuclear distance less than  $1.40a_0$ .

For purpose of our vibrational averaging, the method of least squares has again been employed to obtain a power-series expansion of our calculated  $\chi_1^p(R)/R^2$  about the equilibrium distance.

#### IV. RESULTS AND DISCUSSION

In Table IV, we have tabulated our calculated values of  $\langle\chi_1^d\rangle$ ,  $\langle\chi_{11}^d\rangle$ ,  $\langle\chi_1^p\rangle$ , and  $\langle\chi\rangle$  for comparison with experiment. Values are given for H<sub>2</sub>, HD, and D<sub>2</sub> in a number of vibrational-rotational states. Where applicable, the results of Auffray are also listed. For sake of clarification, we point out that Auffray's value<sup>34</sup> for  $\langle\chi\rangle_{0,1}$  is based upon a calculation employing Ramsey's experi-

<sup>34</sup>  $\langle O\rangle_{0,1}$  denotes an average of the property  $O$  over the vibrational state  $v=0$  and the rotational state  $J=1$ .

TABLE V. The rotational  $g$  values of  $H_2$ .

	$H_2$			HD		$D_2$	
	$R_e$	$v=0, J=1$	$v=0, J=2$	$R_e$	$v=0, J=1$	$R_e$	$v=0, J=1$
$g_J^e$ Present work	-0.07625	-0.08250	-0.08300	-0.05720	-0.06118	-0.03815	-0.04027
$g_J^e$ Espe <sup>e</sup>	-0.09705	-0.11614	-0.11673	-0.07280	-0.08503	-0.04855	-0.05509
$g_J^e$ Experiment		-0.11709	-0.11774		-0.08691		-0.05736
		$\pm 0.00007^a$	$\pm 0.00004^a$		$\pm 0.00001^b$		$\pm 0.00005^a$
$g_J$ Present work	0.92375	0.91750	0.91700	0.69292	0.68894	0.46210	0.45998
$g_J$ Espe	0.90295	0.88386	0.88327	0.67732	0.66509	0.45170	0.44516
$g_J$ Experiment		0.88291	0.88227		0.66321		0.44288
		$\pm 0.00007^a$	$\pm 0.00004^a$		$\pm 0.00001^b$		$\pm 0.00005^a$

<sup>a</sup> R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. 94, 893 (1954).

<sup>b</sup> W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, Phys. Rev. 112, 1929 (1958).

<sup>c</sup> I. Espe, Phys. Rev. 103, 1254 (1956).

mental rotational moments and assuming his functional dependence of the rotational moment upon internuclear distance. Also shown are the results of a vibrational averaging of Espe's  $\chi_{1^p}$ 's. Here, the motional averaging was performed after fitting his values of  $\chi_{1^p}$  at the three internuclear separations to a parabola.

To illustrate the order of magnitude of vibrational effects on the magnetic properties under consideration, values of the susceptibilities at the equilibrium internuclear separation are also included in Table IV. It is seen that the effect of zero-point vibration on  $\chi_{11^d}$  and  $\chi_{1^d}$  is only about 2-3% and is therefore not very marked. In contrast,  $\chi_{1^p}$  is a sensitive function of the internuclear distance. For this quantity, there is a correction of almost 20% due to the influence of zero-point motion. This appears to be true with both Espe's result and our one-parameter calculation using the zeroth-order wave function of Kolos and Roothaan. The much stronger  $R$  dependence of  $\chi^p$  as compared to  $\chi^d$  is understandable, since  $\chi^p$  involves the angular momentum operator and is therefore more sensitive to small changes in the shape of the charge distribution. The effects of zero-point vibration on the total susceptibility and the rotational

magnetic moment is not pronounced (at most a few percent) as both of these quantities contain large contributions which are either independent of or not strongly dependent upon the internuclear separation. As expected, the vibrational correction in the first excited vibrational state is in all cases roughly three times as large as the effect of zero-point motion, and the effect of centrifugal stretching introduces a small correction of an order of magnitude smaller than that due to zero-point vibration.

In Table V, theoretical values of  $g_J$  and  $g_J^e = \langle \mu_R^e \rangle / J \mu_N$  for  $H_2$ , HD, and  $D_2$  are listed for comparison with experiment. These expectation values have been obtained for the  $v=0, J=1$  state and for  $H_2$ , also for the  $v=0, J=2$  state. From these results, it is clear that motional averaging leads to improvements in the direction of agreement with experiment. The theoretical values of  $\langle g_J \rangle$ , both those obtained using Espe's  $\chi_{1^p}$  and our  $\chi_{1^p}$ , are in fairly good agreement with experiment, the results from Espe's calculation being somewhat better as expected. However, since  $\langle g_J \rangle$  in this case involves a large contribution from a nuclear term, it is by itself not a very sensitive test of the accuracy of *ab initio* calculations. Instead, one has to consider  $\langle g_J^e \rangle$ .

In Table VI, we have tabulated ratios of  $\langle g_J^e \rangle_{0,1}$  between pairs of molecules for comparison with experiment. The corresponding ratio for  $H_2$  in its  $v=0, J=1$ , and  $v=0, J=2$  states is also given. It is gratifying to

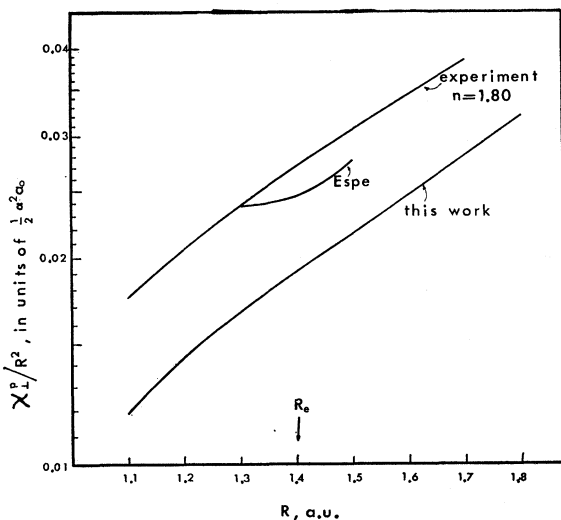


FIG. 1. The variation of  $\chi_{1^p}^p / R^2$  with internuclear distance.

TABLE VI. Ratios and differences of  $\langle g_J^e \rangle$ .

	Present work	Espe's	Experiment	Reduced-mass ratio
$H_2 \langle g_J^e \rangle_{0,1}$	0.9940	0.9949	0.9945	1.00000
$H_2 \langle g_J^e \rangle_{0,2}$			$\pm 0.0009$	
$H_2 \langle g_J^e \rangle_{0,1}$	1.3484	1.3659	1.3472	1.33311
HD $\langle g_J^e \rangle_{0,1}$			$\pm 0.001$	
$H_2 \langle g_J^e \rangle_{0,1}$	2.0486	2.1082	2.0412	1.99901
$D_2 \langle g_J^e \rangle_{0,1}$			$\pm 0.003$	
HD $\langle g_J^e \rangle_{0,1}$	1.5193	1.5435	1.5151	1.49950
$D_2 \langle g_J^e \rangle_{0,1}$			$\pm 0.002$	
$H_2 \langle g_J^e \rangle_{0,1} - HD \langle g_J^e \rangle_{0,1}$	-0.02132	-0.03111	-0.03018	
$H_2 \langle g_J^e \rangle_{0,1} - D_2 \langle g_J^e \rangle_{0,1}$	-0.04223	-0.06105	-0.05973	
$HD \langle g_J^e \rangle_{0,1} - D_2 \langle g_J^e \rangle_{0,1}$	-0.02091	-0.02994	-0.02955	



note the excellent agreement between our predicted ratios and the experimental ratios. It is also interesting that the ratios predicted by Espe's calculation are in considerably poorer agreement with experiment. In Table VI, we have listed in the last column the appropriate reduced mass ratios, which in the absence of vibrational motion would account for the ratios of the rotational moments. These values are significantly different from our theoretical ratios including the effect of nuclear motion.

The excellent agreement between theory and experiment depicted in Table VI, suggests in the light of the inaccuracies of our electronic calculations of the high-frequency terms using a one-parameter variation function, that the true  $\mu_{R^e}(R)$  and  $\chi_{1^p}(R)$  curves (semilog plots) are merely displaced from the calculated curves without change in shape, at least for small vibrational displacements. This point appears to be confirmed by the plots in Fig. 1, where our calculated curve for  $\chi_{1^p}/R^2$  is compared with the variation with internuclear distance inferred from Ramsey's molecular beam experiments. The constancy of  $\langle g_{J^e} \rangle$  experiment  $\langle g_{J^e} \rangle$  calculated depicted in Table VII is also in accord with our present contention.

TABLE VII.  $\langle g_{J^e} \rangle$  experiment/ $\langle g_{J^e} \rangle$  calculated.

		Without vibrational averaging	After vibrational averaging
H <sub>2</sub>	$v=0, J=1$	1.5355	1.4192
	$v=0, J=2$	1.5355	1.4185
HD	$v=0, J=1$	1.5194	1.4205
D <sub>2</sub>	$v=0, J=1$	1.5038	1.4244
		Average $1.421 \pm 0.002$	

Since one uses the differences in the rotational magnetic moments of isotopic molecules in the determina-

tion of dipole moments, it is instructive to compare the differences in the  $\langle g_{J^e} \rangle$ 's for H<sub>2</sub>, HD, and D<sub>2</sub> with experiment. These results are given in Table VI. It is seen that the results from Espe's calculation agree very closely with experiment. Our own results, however, are all a factor of 1.421 less than the experimental differences.

All the results presented in this section are for the Morse oscillator. Slightly different numbers are obtained with the Dunham potential. However, the same general conclusions prevail. Differences between the two sets of figures are generally of the order of magnitude of centrifugal corrections.

## V. CONCLUSIONS

The results of the present work can have the following implications. First, the success with which we have been able to predict the variations of  $\chi_{1^p}/R^2$  with internuclear distance suggests that in general the variation of this quantity with  $R$  can be accurately obtained by a simple variational calculation provided accurate zero-order wave functions are available for many internuclear distances. Since by this procedure, their absolute values will generally not be obtainable accurately, ratios of the  $\langle \chi_{1^p}/R^2 \rangle$ 's for different isotopic species are more reliable than their differences. The dipole moments of some heteronuclear diatomic molecules are sometimes determined by variations of the rotational  $g$  values upon isotopic substitution neglecting the effects of vibrational motion. In view of the relatively large vibrational corrections for the high-frequency part of the susceptibility, reliable dipole moments of these heteronuclear diatomic molecules cannot be obtained from molecular-beam magnetic resonance data without vibrational corrections. If such corrections are to be made by an *ab initio* calculation of the  $R$  dependence of  $\chi_{1^p}$ , then the dipole moment of the molecule,  $\mu_e$ , should be obtained from the following ratio equation:

$$\frac{\left\langle \frac{\chi_{1^p}}{R^2} \right\rangle_{AB}}{\left\langle \frac{\chi_{1^p}}{R^2} \right\rangle_{A'B}} = \frac{\left\{ \frac{\xi_A \xi_B}{\xi_A + \xi_B} - 2 \left\langle \frac{\mu_e}{Re} \right\rangle_{AB} \left( \frac{M_B}{M_A + M_B} - \frac{\xi_B}{\xi_A + \xi_B} \right) - \left\langle \frac{\mu_e^2}{R^2 e^2} \right\rangle_{AB} \frac{1}{\xi_A + \xi_B} - \frac{\langle \mu_R \rangle_{AB}}{J \mu_N} \mu_{AB'} \right\}}{\left\{ \frac{\xi_A \xi_B}{\xi_A + \xi_B} - 2 \left\langle \frac{\mu_e}{Re} \right\rangle_{A'B} \left( \frac{M_B}{M_{A'} + M_B} - \frac{\xi_B}{\xi_A + \xi_B} \right) - \left\langle \frac{\mu_e^2}{R^2 e^2} \right\rangle_{A'B} \frac{1}{\xi_A + \xi_B} - \frac{\langle \mu_R \rangle_{A'B}}{J \mu_N} \mu_{A'B'} \right\}} \quad (20)$$

instead of the usual difference equation.<sup>12</sup> Considerations of this nature are currently progress for HF, where there is presently a discrepancy (about 7%) in the values of the dipole moments obtained from molecular beam electric resonance<sup>35</sup> and from the rotational moments<sup>36</sup> of HF and DF. In a separate communication, we shall show how this discrepancy can be resolved employing the approach suggested above.

<sup>35</sup> R. E. Weiss, MIT dissertation, 1961 (unpublished).

<sup>36</sup> M. R. Baker, C. H. Anderson, J. Pinkerton, and N. F. Ramsey, Bull. Am. Phys. Soc. 6, 19 (1961).