

**Numerical coupled Hartree–Fock study of the total (electronic and nuclear) parallel polarizability and hyperpolarizability for the FH, H+ 2, HD+, and D+ 2 molecules**

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# Numerical coupled Hartree–Fock study of the total (electronic and nuclear) parallel polarizability and hyperpolarizability for the FH, H<sub>2</sub><sup>+</sup>, HD<sup>+</sup>, and D<sub>2</sub><sup>+</sup> molecules<sup>a)</sup>

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Polarizabilities and hyperpolarizabilities of molecules have both electronic and vibrational contributions. The latter can be important in experimental determinations involving static electric fields, as in the Kerr effect. This paper reports purely numerical coupled Hartree–Fock calculations for the electronic states of FH. Electronic energy surfaces obtained for different electric field strengths are then used to solve, numerically, the nuclear equation for several vibrational states. The vibrational contributions to  $\beta_{zzz}$  exceed the electronic component and change the sign of the total hyperpolarizability.  $\gamma_{zzzz}$  is similarly increased by an order of magnitude. It is also shown that a Born–Oppenheimer treatment of H<sub>2</sub><sup>+</sup> for  $\gamma_{zzzz}$  is in perfect agreement with a recent fully nonadiabatic three particle solution.

## I. INTRODUCTION

When a molecule is exposed to an external electric field a complicated polarization process takes place. The cloud of the electronic charge is deformed to accommodate the external field and, simultaneously, the vibrational molecular motion is perturbed by the change in the electronic potential. The coupling between the deformations of electronic and nuclear structure has been studied within the harmonic oscillator approximation by Pandey and Santry.<sup>1</sup> Also Bishop, Cheng, and Buckingham<sup>2</sup> have noted this problem and have performed a calculation of the total molecular polarizability for the H<sub>2</sub> molecule with a sum-over-state perturbation method which simultaneously accounts for both electronic and nuclear perturbations. This phenomena has also been considered by Elliot and Ward.<sup>3</sup>

It should be noted that there is more than one type of vibrational correction. To illustrate, using the harmonic oscillator approximation, Pandey and Santry,<sup>1</sup> derived formulas for vibronic contributions for molecular polarizabilities and hyperpolarizabilities. The appropriate expression for a  $\beta$  hyperpolarizability component for a diatomic molecule has the following two dominant terms:

$$\beta_v = \frac{1}{4a^2} \left( \frac{\partial^2 \beta}{\partial R^2} \right)_0 + \frac{3}{a^2 \hbar \omega} \left( \frac{\partial \mu}{\partial R} \right)_0 \left( \frac{\partial \alpha}{\partial R} \right)_0, \quad (1)$$

where

$$\alpha = (m\omega/\hbar)^{1/2},$$

$m$  is the reduced mass,  $\omega$  the frequency of the vibration,  $\mu$  the dipole moment, and  $\alpha$  the polarizability. The above formula is for a diatomic system, which remains in its ground vibrational level. The first term in Eq. (1) results from averaging the hyperpolarizability over the first vibrational state and corresponds to what is usually called the vibrational average. The second term depends upon the first derivatives of the dipole moment and the polarizability with respect to the bond distance and reflects the interaction of the applied field

with the vibrational structure of the molecule, which leads to small changes in the molecule's geometric structure and shifts in its vibrational levels.

Using the above formulas, Lazzeretti *et al.*<sup>4</sup> estimated that for the FH molecule the vibrational correction to the static Hartree–Fock hyperpolarizability  $\beta_{zzz}$  component ( $z$  is the molecular axis) is as large as 10.5 a.u. Utilizing Lazzeretti's value for the second derivative of  $(\partial^2 \beta_{zzz}/\partial^2 R)$  one can estimate that the first term in Eq. (1) is equal to  $-2.15$  a.u. This brings us to the conclusion that the total vibrational contribution to the hyperpolarizability  $\beta_{zzz}$  is dominated by the second term, which is not obtained within an ordinary vibrational averaging procedure. Instead, from the viewpoint of perturbation theory, this term derives from vibrational excited states in a sum-over-states formula.<sup>3</sup>

Taking previously determined SCF results for  $\beta_{zzz}$  for the electronic contribution<sup>5,6</sup> and adding the nuclear correction, one should expect the total SCF  $\beta_{zzz}$  hyperpolarizability component for FH to be positive with a value around 2 a.u. Such a large nuclear contribution to the first molecular hyperpolarizability, contrary to the rather small corrections to the dipole moment and polarizability, is a physically significant phenomenon for static fields. Since previous extensive correlated results<sup>6,7</sup> have established that  $\beta_{zzz} \gg \beta_{xxx}$  for FH, such an effect could make an important contribution to the static value of

$$\chi_{\parallel}^{(2)}(0;0,0) = 3/10(\beta_{zzz} + 2\beta_{xxx}).$$

However, as long as  $\chi_{\parallel}^{(2)}$  is determined at optical frequencies [as is done in dc-induced second-harmonic generation (DC-SHG) experiments  $\chi_{\parallel}^{(2)}(-2\omega;\omega,\omega)$ ; for example, see Ref. (8)], such nuclear perturbations are negligible.<sup>3</sup> On the other hand, for

$$\chi_{\parallel}^{(3)}(-2\omega;0,\omega,\omega) = 1/6(1/5\gamma_{yyzz} + 4/5\gamma_{yyzz} + 8/15\gamma_{yyyy})$$

and in the Kerr effect,  $\chi(-\omega;0,\omega)$ ,<sup>9</sup> the presence of the static field ( $\omega = 0$ ) raises the question of the importance of such vibrational contributions.

In this paper, numerical Hartree–Fock calculations on the total response of the FH molecule and the H<sub>2</sub><sup>+</sup> cation to

<sup>a)</sup> This work has been supported by the United States Air Force Office of Scientific Research.

the electric field are presented to assess the importance of vibrational corrections to  $\beta_{zzz}$  and  $\gamma_{zzzz}$ . The Born–Oppenheimer approximation is employed and both a Schrödinger equation for electrons with the field and the nuclear vibrational equation are solved numerically. The parallel components of the polarizabilities are calculated by numerical differentiation of the total molecular energy with respect to the field strength. The perturbation of the nuclear vibrational motion by the field is analyzed and it is shown that vibrational levels are shifted along with the position of the internuclear equilibrium. In addition, contrary to a recent paper<sup>10</sup> that proposed that nonadiabatic corrections for  $H_2^+$  are important in the second hyperpolarizability for  $H_2$ , we show that  $\gamma_{zzzz}$  is entirely explained by a Born–Oppenheimer treatment.

## II. MOLECULAR POLARIZABILITIES

The total energy of an uncharged molecule in an external field can be written in a power series as

$$W(F) = W(0) - \mu_i F_i - (2!)^{-1} \alpha_{ij} F_i F_j - (3!)^{-1} \beta_{ijk} F_i F_j F_k - (4!)^{-1} \gamma_{ijkl} F_i F_j F_k F_l, \quad (1a)$$

where summation over repeated indexes is assumed.  $F_i$  is a component of the external field,  $\mu_i$  is a component of the permanent dipole moment,  $\alpha_{ij}$  a dipole polarizability, and  $\beta_{ijk}$  the first, and  $\gamma_{ijkl}$ , the second hyperpolarizability. For a diatomic system with the field orientation parallel to the bond axis  $z$  (we confine our present consideration to this case only), the expansion in Eq. (1a) simplifies to

$$W(F_z) = W(0) - \mu F_z - (2!)^{-1} \alpha_{zz} F_z^2 - (3!)^{-1} \beta_{zzz} F_z^3 - (4!)^{-1} \gamma_{zzzz} F_z^4 - \dots \quad (2)$$

The total molecular energy  $W$  is a sum of electronic and nuclear contributions. Therefore, in our definition the expansion coefficients  $\mu$ ,  $\alpha$ ,  $\beta$ , etc., are not, as usually assumed, only electronic quantities, but they reflect both electronic and nuclear polarization of the system.

To determine  $W$ , the Schrödinger equation with the field for the coupled electron–nuclear motion should be solved. Computationally, this poses a very difficult task. However, when the Born–Oppenheimer approximation is imposed and the total wave function is written as a product of an electronic and nuclear part,

$$\psi(\bar{r}; \bar{R}) = \psi_e(\bar{r}; \bar{R}) X_n(\bar{R}) \quad (3)$$

and with the usual neglect of small terms the electronic equation separates from the nuclear equation:

$$[T_e + V(\bar{r}; \bar{R})] \psi_e(\bar{r}; \bar{R}) = W_e(\bar{R}) \psi_e(\bar{r}; \bar{R}), \quad (4a)$$

$$[T_n + W_e(\bar{R})] X_n(\bar{R}) = W X_n(\bar{R}). \quad (4b)$$

$T_e$  is the kinetic energy operator and  $V(\bar{r}; \bar{R})$  is the electrostatic potential between all pairs of particles. When the interaction with the field is introduced into the electronic equation, Eq. (4a), the total perturbed molecular energy  $W$  can be evaluated by solving the nuclear equation in which the field-free electronic potential  $W_e(\bar{R})$  is replaced by the field-dependent one.

Finally, the molecular dipole moment, parallel molecular polarizability, and hyperpolarizability, are determined by numerical differentiation of the total energy with respect to the field strength. The appropriate formulas are formally identical as for electronic polarizabilities<sup>6</sup>:

$$\mu_z = 1/F_z \{ -2/3 [W(F_z) - W(-F_z)] + 1/12 [W(2F_z) - W(-2F_z)] \}, \quad (5a)$$

$$\alpha_{zz} = 1/F_z^2 \{ 5/2 W(0) - 4/3 [W(F_z) + W(-F_z)] + 1/12 [W(2F_z) + W(-2F_z)] \}, \quad (5b)$$

$$\beta_{zzz} = 1/F_z^3 \{ -1/2 [W(2F_z) - W(-2F_z)] + [W(F_z) - W(-F_z)] \},$$

$$\gamma_{zzzz} = 1/F_z^4 \{ 4 [W(F_z) + W(-F_z)] - [W(2F_z) + W(-2F_z)] - 6W(0) \}. \quad (5c)$$

Each of these formulas has been obtained by excluding all even or odd terms in Eq. (1a) by using positive and negative fields of the same magnitude. This ensures that the contamination from the next higher term in the power series is completely removed, leaving only the next higher term of the same type (i.e., even or odd) which is a few orders of magnitude smaller (at the field strengths used here) than any polarizability being determined. Hence, essentially no error in the Hartree–Fock polarizabilities is anticipated from higher polarizability contamination. At the same time, however, field strengths of adequate size have been used to ensure that significant energy differences are obtained. In this work, field strengths of 0.0,  $\pm 0.01$ , and  $\pm 0.02$  a.u. are found to be suitable.

TABLE I. First six vibrational levels and the internuclear equilibrium distance calculated with the Hartree–Fock method for the FH molecule for different electric field strengths.

Electric field (a.u.)	$\Delta G_{v+1/2}$						Equilibrium distance (a.u.)
	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$	$v=5$	
	(cm <sup>-1</sup> )						
– 0.02	2263	4393	4235	4082	3935	3795	1.6857
– 0.01	2244	4355	4197	4044	3898	3757	1.6900
0.0	2220	4306	4149	3995	3846	3705	1.6951
+ 0.01	2192	4250	4088	3833	3783	3639	1.7010
+ 0.02	2160	4184	4019	3856	3706	3557	1.7079

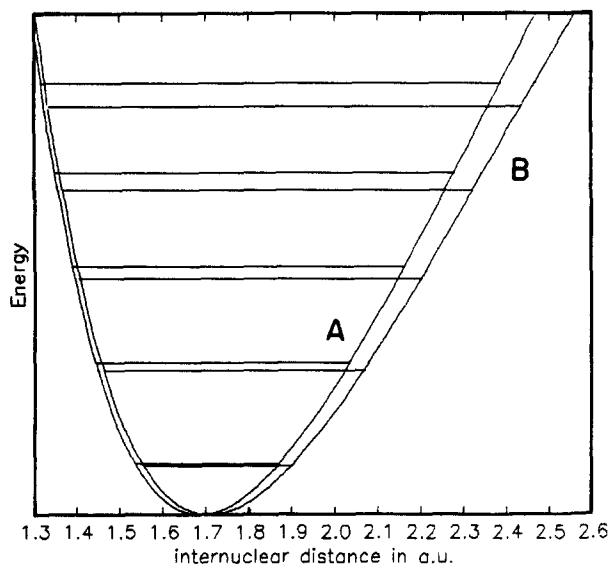


FIG. 1. Comparison of the vibrational structure of the FH molecule exposed to an electric field of strength  $-0.02$  a.u. (curve A) and  $+0.02$  a.u. (curve B).

### III. NUMERICAL DETAILS

The FH molecule is investigated. The electronic Schrödinger equation with the field has been solved in the Hartree-Fock approximation numerically using the procedure, which has been previously applied by Christiansen and McCullough,<sup>5</sup> to determine the exact coupled Hartree-Fock parallel polarizabilities for FH. The procedure utilizes partial wave expansions for molecular orbitals<sup>11</sup> and for all practical purposes the results should be recognized as accurate solutions of the HF equation. The use of numerical molecular orbitals almost eliminates the basis set problem at the Hartree-Fock level, which has been found to be critical for the determination of the electronic hyperpolarizability.<sup>8</sup> Correlation corrections are, of course, still important in any comparison with experiment.<sup>6,7</sup> Calculations for all five different electric field strengths have been performed for internuclear distances ranging from 0.6 to 3.5 a.u. for at least 50 points. This number of points has been found sufficient to stabilize the first vibrational state within  $0.01 \text{ cm}^{-1}$ . Such

accuracy is satisfactory for determining the ground state hyperpolarizability by numerical differentiation. The molecular vibrational equation has been solved numerically using the program DVIBRO originally created by Kirby-Docken and Hinze.<sup>12</sup>

### IV. RESULTS

Structural information presented in Table I and Fig. 1 shows the degree that the nuclear vibrational motion changes for the FH molecule subject to an electric field. When the field alters its direction from  $-0.02$  to  $+0.02$  a.u. (the bond axis orientation is from fluorine to hydrogen) vibrational levels move closer to the bottom of the potential curve. For the first vibrational state, this shift reaches  $100 \text{ cm}^{-1}$  and becomes even larger for higher levels. It is interesting that the position of the equilibrium internuclear separation also drifts with the field and is equal to 1.6857 and 1.7079 a.u. for fields of  $-0.02$  and  $+0.02$  a.u., respectively. This last value is much closer to the experimental field-free ground state internuclear distance of 1.7328 a.u., which has been used by Christiansen and McCullough<sup>5</sup> in their polarizability calculations.

Table II presents dipole moments, polarizabilities, and hyperpolarizabilities determined using different approaches. In the first two columns there are electronic polarizabilities calculated for fixed internuclear distances, which are the experimental equilibrium in the first case and the Hartree-Fock equilibrium in the second. In the last column, total molecular polarizabilities are presented. These have been obtained by numerical differentiation of the total molecular energy in the ground vibrational state. It is seen that the molecular dipole and the molecular polarizability are almost identical to the appropriate electronic quantities at the experimental geometry. However, the molecular hyperpolarizability is dramatically different from the electronic result in both magnitude and sign. Our result for  $\beta_{zzz}$  is equal to  $+1.61$  a.u. and this agrees quite well with the semiempirical estimate obtained with Pandey and Santry's formulas as discussed in the Introduction.

In Table III, molecular dipole moments and polarizabilities calculated for the first six vibrational levels are shown. The systematic increase of the dipole and the polarizability

TABLE II. FH molecule. Electronic Hartree-Fock polarizabilities calculated for the experimental and Hartree-Fock equilibrium distances and total molecular polarizabilities calculated for the first vibrational state. All quantities are in atomic units.

	$R = 1.7328 \text{ a.u.}$ (expt. equilibrium)	$R = 1.6951 \text{ a.u.}$ (HF equilibrium)	$v = 0$
Dipole moment	0.756	0.741	0.753
Polarizability	5.75	5.55	5.93
Hyperpolarizability ( $\beta_{zzz}$ )	$-8.5^a$	$-7.6$	1.6
Second hyperpolarizability ( $\gamma_{zzzz}$ )	$270 \pm 10^a$	$230 \pm 10$	$1720 \pm 10$

<sup>a</sup>The difference between our results and the results reported by Christiansen and McCullough (Ref. 5) is probably due to the different numerical differentiation procedure and different field strengths applied. In the present paper, more accurate symmetric formulas for the numerical differentiation have been used.

TABLE III. FH molecule. Hartree–Fock molecular dipole moments and polarizabilities calculated for the first six vibrational levels. All quantities are in atomic units.

	Vibrational levels					
	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$	$\nu = 5$
Dipole moment	0.75	0.78	0.80	0.83	0.85	0.88
Polarizability	5.9	6.2	6.8	7.4	7.9	8.6

with vibrational excitation for the FH molecule should be experimentally verifiable by performing measurements at different temperatures. The more populated the higher excited vibrational states become, the larger the molecular dipole moment and the molecular polarizability will be. The dependence of the hyperpolarizability on the vibrational state is not presented because the energy of higher vibrational levels is not determined to sufficient accuracy. Moreover, higher vibrational states are more subject to the well-known deficiency of the Hartree–Fock method in describing the dissociation.

One may ask how much of a nonadiabatic character is present in  $\gamma_{zzzz}$ ? Recent three-body calculations by Bishop and Solunac<sup>10</sup> for the  $H_2^+$  ion provide an opportunity to examine this effect. The electronic parallel second hyperpolarizability for  $H_2^+$  in the Born–Oppenheimer approximation for the fixed internuclear distance of 2.0 a.u. is equal to  $-41$  a.u. The inclusion of the nuclear motion and departure from the adiabatic approximation dramatically alters the result making it equal to  $2.2 \times 10^3$  a.u.<sup>10</sup> Bishop and Solunac attribute this drastic change partly to the nonadiabaticity of  $\gamma_{zzzz}$ . Our calculations for the polarizability and second hyperpolarizability of  $H_2^+$  performed with the current procedure give results which entirely contradict the conclusion drawn by Bishop and Solunac. As seen in Table IV, our Born–Oppenheimer results are almost identical with their nonadiabatic ones. An optimistic conclusion which emerges from this is that the second molecular hyperpolarizability can still be calculated with electronic and nuclear motion kept separate, without resorting to a complicated nonadiabatic treatment, but does require proper inclusion of vibrational motion.

## V. SUMMARY

It has been shown that the vibrational contribution to the molecular hyperpolarizability of FH is of the same order of magnitude as the electronic contribution, but has an opposite sign. This is not the case for the molecular dipole moment and the molecular dipole polarizability. The present study suggests that it is necessary to account for the deformation of the nuclear frame simultaneously with the electronic deformation to determine accurate static molecular hyperpolarizabilities. These might be important when considering nonlinear optical phenomena that are generated when using a static field. The present results, obtained in the Born–Oppenheimer approximation with the Hartree–Fock method, are subject to errors originating from the approximations applied. However, it seems likely that the error

TABLE IV. Born–Oppenheimer results for the total molecular polarizabilities ( $\alpha_{zz}$ ) and hyperpolarizabilities ( $\gamma_{zzzz}$ ) of  $H_2^+$ ,  $HD^+$ , and  $D_2^+$  calculated for the first three vibrational levels (in atomic units).

	Present results		Nonadiabatic results of Bishop and Solunac (Ref. 10)	
	$\alpha_{zz}$	$\gamma_{zzzz}$	$\alpha_{zz}$	$\gamma_{zzzz}$
$H_2^+$				
$\nu = 0$	5.84	$2.3 \times 10^3$	5.83	$2.2 \times 10^3$
$\nu = 1$	7.70	$4.8 \times 10^3$		
$\nu = 2$	10.14	$9.8 \times 10^3$		
$HD^+$				
$\nu = 0$	5.72	$2.2 \times 10^3$	5.72	$2.1 \times 10^3$
$\nu = 1$	7.28	$4.1 \times 10^3$		
$\nu = 2$	9.24	$7.7 \times 10^3$		
$D_2^+$				
$\nu = 0$	5.59	$2.0 \times 10^3$	5.59	$2.0 \times 10^3$
$\nu = 1$	6.81	$3.5 \times 10^3$		
$\nu = 2$	8.27	$5.8 \times 10^3$		

which originates with the separation of the nuclear and electronic motions is insignificant for the first and second molecular static hyperpolarizabilities.

Elsewhere, we have reported extensively correlated studies of all components of the hyperpolarizabilities of FH,<sup>6,7</sup> and correlation can change the Hartree–Fock values by almost 100%. We have also considered effects of frequency dependence at the time-dependent Hartree–Fock level for a variety of nonlinear optical processes.<sup>13</sup> We have also used numerical orbital techniques<sup>14</sup> in a correlated study of the  $\beta_{zzz}$  and  $\gamma_{zzzz}$  hyperpolarizability components.<sup>15</sup> These studies attempt to assess the importance of electron correlation and frequency dependence in comparison with experiment.<sup>8</sup>

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