Molecules in Electric Fields

I. The Polarisability of the Hydrogen Molecule

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Finite field perturbation theory coupled with configuration interaction techniques have been used to evaluate the components of the polarisability tensor of H_2 at and near its equilibrium internuclear separation. The values are fitted to a polynomial which then yields the derivatives of the polarisability with respect to internuclear distance. Our results compare favourably with theoretical values obtained by the use of highly accurate correlated wavefunctions.

Introduction

The behaviour of atoms and molecules in an electric field is the subject of considerable interest from both the experimental and theoretical points of view. Most theoretical approaches to date have been based on the Hartree-Fock self consistent field theory coupled with a perturbation treatment [1–3], although for two-electron systems such as the helium atom and the hydrogen molecule it has been possible to carry out very accurate calculations using correlated wavefunctions [4–6]. Configuration interaction (CI) and multiconfigurational self-consistent field (MCSCF) approaches have not been systematically explored in polarisability calculations, although recently some progress has been made in this direction by Watts and Buckingham [7, 8]. The desirability of such calculations was indicated by Kolker and Karplus [3] a decade ago and even earlier by Hirschfelder [9], suggesting that severe overestimation of the parallel component of the polarisability of a diatomic molecule occurs if the Hartree-Fock wavefunction is used for the unperturbed ground state, since that type of function does not lead to the correct separated atom limit. The aim of the present work is to initiate CI and MCSCF type work to calculate polarisabilities and polarisability gradients. Only a few calculations of polarisability gradients have so far been made, despite their importance in infra-red and Raman spectroscopy. The recent semiempirical work of Hush and Williams [10] aimed at filling this gap, by calculating the polarisability gradients of a number of diatomic molecules. It became apparent, however, that their work needs to be supported and extended by *ab initio* calculations. To make a start in this direction the H_2 molecule was selected as the first example, since for this molecule Kołos and Wolniewicz [6] have obtained highly accurate theoretical values which can be used very conveniently for comparison purposes. The approach we adopted is to obtain

reasonably accurate full CI wavefunctions for the ground state as well as those excited states of the H_2 molecule that are involved in the Rayleigh-Schrödinger second order perturbation expression for a given polarisability tensor component. The basis functions used for this purpose are mixed sets comprising of $1s$ Slater type orbitals and Gaussian functions.

Computational Methods

Consider a set of basis functions $\{\phi_i\}$ (assumed to be orthonormal-symmetry orbitals) which are used to construct the normalized two-electron unperturbed ground state ($^1\Sigma_g^+$) wavefunction, hence given as

$$\Psi_0 = \sum_i y_i Y_i$$

where $\{Y_i\}$ is the full set of configurations of $^1\Sigma_g^+$ symmetry and $\{y_i\}$ is the set of variational constant coefficients. A typical configuration is given as

$$Y_i = \mathscr{A}\{[\phi_k(1)\,\phi_l(2)]\,2^{-\frac{1}{2}}\,[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)]\}\,,$$

where $\mathscr{A}$ is the antisymmetrizer and α and β are the spin functions.

In the presence of a field parallel to the molecular axis the point group of the molecule becomes $C_{\infty v}$ and the Hamiltonian is now given as

$$\mathscr{H} = \mathscr{H}_0 + F(z_1 + z_2)$$

where $\mathscr{H}_0$ is the unperturbed Hamiltonian (within the Born-Oppenheimer approximation).

F is the electric field strength and z_1 and z_2 are the dipole moment operators for electrons 1 and 2.

The total, normalized wavefunction is now written as

$$\Psi = \sum_i C_i \Phi_i$$

where $\{\Phi_i\}$ now includes the set $\{Y_i\}$ but contains in addition all the possible configurations of $^1\Sigma_u^+$ symmetry as well and $\{C_i\}$ is the set of variational constants for a given field F.

Let

$$E(F) = \langle \Psi | \mathscr{H} | \Psi \rangle$$

and

$$E_0 = \langle \Psi_0 | \mathscr{H}_0 | \Psi_0 \rangle\,.$$

The parallel component of the polarisability tensor is defined as

$$\alpha_\| = \alpha_{zz} = -(\partial^2 E(F)/\partial F^2)_{F=0}\,,$$

and since to second order

$$E(F) = E_0 - \tfrac{1}{2}\,\alpha_\| F^2\,,$$

$\alpha_\|$ can be calculated from the limiting slope of the plot of $E(F)$ $vs.$ F^2. This approach to the calculation of a given polarisability component is known as Finite Field Perturbation.

In the presence of a field F perpendicular to the molecular axis the total wave-function Ψ must include all the possible $^1\Pi_u^+$ configurations since the Hamiltonian is now

$$\mathscr{H} = \mathscr{H}_0 + F(x_1 + x_2).$$

Hence the perpendicular component of the polarisability tensor can be calculated as described above using the expression

$$E(F) = E_0 - \tfrac{1}{2}\alpha_\perp F^2.$$

Since

$$\alpha_\perp = \alpha_{xx} = \alpha_{yy},$$

the average static polarisability α is given as

$$\alpha = \frac{1}{3}(\alpha_\| + 2\alpha_\perp).$$

Using Rayleigh-Schrödinger perturbation theory one obtains the following expressions which define the two polarisability components:

$$\alpha_\| = 2\sum_n \frac{|\langle\Psi_0|\,x_1 + x_2\,|X_n\rangle|^2}{E_n - E_0}$$

where $\{X_n\}$ is the set of $^1\Sigma_u^+$ type wavefunctions and $\{E_n\}$ is the corresponding set of energies;

$$\alpha_\perp = 2\sum_n \frac{|\langle\Psi_0|\,x_1 + x_2\,|Z_n\rangle|^2}{E_n - E_0}$$

where $\{Z_n\}$ is the set of $^1\Pi_u^+$ type wavefunctions with $\{E_n\}$ as the corresponding set of energies.

It is clear from the above expressions that in order to obtain good values of $\alpha_\|$ and $\alpha_\perp$ one needs to have good Σ_u and Π_u type excited state as well as good ground state wavefunctions. To achieve this we have used a basic set of functions whose orbital exponents were chosen so as to minimize the ground state energy after which the basis was expanded by Gaussian functions whose orbital exponents were optimized so as to minimize the energy of the lowest excited state $(\Sigma_u$ or $\Pi_u)$, since that state is expected to have the greatest effect on the given polarisability component.

In the actual computations a set of Schmidt orthogonalized symmetry orbitals were constructed (which transform according to the irreducible representations of the $D_{\infty h}$ point group) from the given set of Slater and Gaussian functions. The orthonormal orbitals were then used to construct the set of configurations. Most of the computational details have been fully described previously [11, 12]. In the calculation of mixed one-electron integrals 10 Gaussians were used per Slater orbital; in the case of two-electron integrals the number of Gaussians was 4. The expansion constants are those given by Huzinaga et al. [13]. The polarisability in each case was calculated by both the Rayleigh-Schrödinger and the finite field perturbation methods. In all calculations complete agreement was found to four significant figures.

Table 1. The orbital bases used in the various calculations at an internuclear separation of 1.4 a.u.

$s_A(1.1005)$, $s_B(1.1005)$, $s'_A(1.6331)$, $s'_B(1.6331)$ $G_0(1.0860)$	Basic 5 orbital basis
$G_A(0.42)$, $G_B(0.42)$	Additional orbitals used in the 7 orbital calculation of α
$G_A(0.42)$, $G_B(0.42)$, $G'_A(1.80)$, $G'_B(1.80)$	Additional orbitals used in the 9 orbital calculation of α
$p_{x_A}(0.04)$, $p_{x_B}(0.04)$	Additional orbitals used in the 7 orbital calculation of α
$p_{x_A}(0.04)$, $p_{x_B}(0.04)$, $p'_{x_A}(0.175)$, $p'_{x_B}(0.175)$	Additional orbitals used in the 9 orbital calculation of α

$s = 1s$-type Slater orbital, $G = 1s$-type Gaussian function. The subscripts A, B, 0 refer to nuclei A, B and the midpoint of the internuclear axis respectively. p_x is a normalized Gaussian lobe function, given as

$$p_x(a) = N \exp\{-a[(x-0.1)^2 + y^2 + z^2]\} - N \exp\{-a[(x+0.1)^2 + y^2 + z^2]\},$$

N being the normalization constant.
The orbital exponents are given in brackets.

By extension of the above treatments it becomes possible to evaluate the various principal components of the hyper-polarisability tensor γ. However, the results obtained are not thought to be definitive and sufficiently accurate to merit publication. To calculate γ one needs much more accurate, directly correlated wavefunctions.

All the calculations reported here were carried out on the CDC 6600 digital computer of Control Data Aust. Pty. Ltd., North Sydney.

Calculations and Results

The orbital bases used in the various calculations are listed in Table 1. In order to calculate $\alpha_{\parallel}$ the basic 5 orbital basis was extended by the addition of Gaussians centred on the nuclei to give the 7 and 9 orbital bases. The orbital exponents of these additional functions were successively optimized with respect to the energy of the lowest lying $^1\Sigma_u^+$ state. Calculations of $\alpha_{\perp}$ were carried out in an analogous manner, using normalized Gaussian lobe functions of p_x symmetry on both nuclei. The results of the calculations are summarized in Table 2. The enlargement of the 5 orbital basis brings about a significant improvement in the energy of the lowest $^1\Sigma_u^+$ state but a much smaller improvement in the ground state energy, the latter lying close to the Σ limit of -1.160868 a.u. [14]. The best calculated value of $\alpha_{\parallel}$ is actually higher than the "true" value of 6.383 (calculated by Kołos and Wolniewicz [6]). The addition of more σ-type molecular orbitals to the basis could make this figure a little lower or higher even, eventually resulting in a limiting value that could be obtained by the use of a complete set of σ functions. (In a subsequent calculation it was found that the effect of two more σ-type molecular orbitals was to lower $\alpha_{\parallel}$ to approximately 6.36, showing the non-monotonic nature of the convergence). In the case of $\alpha_{\perp}$, the introduction of the first set of π functions, although resulting in a reasonably

Table 2. Summary of the various calculations at an internuclear separation of 1.4 a.u.

Number of basis functions	Number of $^1\Sigma_g^+$ type configurations	Number of $^1\Sigma_u^+$ or $^1\Pi_u^+$ type configurations	Energy of lowest $^1\Sigma_g^+$ state (a.u.)	Energy of lowest $^1\Sigma_u^+$ or $^1\Pi_u^+$ state (a.u.)	$\alpha_{\parallel}$ (a.u.)	$\alpha_{\perp}$ (a.u.)
5	9	6	−1.158938	−0.524153	5.413	
7	16	12	−1.159700	−0.622699	6.250	
9	25	20	−1.160283	−0.636925	6.399	
7	11	5	−1.158952	−0.672514		1.784
9	15	10	−1.160407	−0.678235		4.506

good value for the energy of the lowest $^1\Pi_u^+$ state, does not produce a reasonable value for $\alpha_{\perp}$. However this is remedied once the second set of π orbitals is introduced. Curiously, the energy of the lowest $^1\Pi_u^+$ state was calculated to be lower than the energy of the lowest $^1\Sigma_u^+$ state, probably as a result of some angular correlation having been allowed for in the former case.

In order to study the behaviour of the two polarisability components with internuclear distance and to calculate the polarisability gradients, the two 9 orbital basis sets were used. The orbital exponents were varied according to the equation:

$$a_i(R) = a_i(R_0) \left[1 - 0.2(R - R_0) \right]$$

where $a_i(R)$ is a given orbital exponent at an internuclear distance R and R_0 is the equilibrium internuclear separation (1.4 a.u.).

Consequently, the variation in orbital exponents is by a constant factor of 0.98 for an increase of 0.1 a.u. in the internuclear separation; it was chosen on the basis of a H_2 calculation by McLean et al. [15], who optimized the orbital exponents at a number of internuclear distances. The results are summarized in Table 3. Use of the above scaling procedure resulted in energy levels with curvatures close to the accurate values as calculated by Kołos and Roothan [16].

$\left(\text{By correct curvature correct behaviour of } \dfrac{\partial E}{\partial R} \text{ vs. } R \text{ is meant.}\right)$

Using the more usual scaling procedure, i.e.

$$a_i(R) = a_i(R_0) R_0/R$$
$$\approx a_i(R_0) \left[1 - 0.72(R - R_0) \right] \quad \text{for} \quad R \approx R_0,$$

the curvature of the energy level of the lowest $^1\Sigma_u^+$ state was too large, leading to too great a variation in $\alpha_{\parallel}$.

The variation of polarisability with internuclear distance is best expressed as a power series, hence the results of Table 3 were fitted to the following polynomial using a least squares procedure:

$$\alpha(R) = a + b(R - R_0) + c(R - R_0)^2 + d(R - R_0)^3 .$$

The constant a is the polarisability at the equilibrium internuclear separation R_0, b, $2c$, and $6d$ are the first, second and third polarisability gradients re-

Table 3. Parallel and perpendicular components of the static polarisability of H_2 at different values of the internuclear separation, calculated using the 9 orbital basis sets

Internuclear separation (a.u.)	$\alpha_{\parallel}$ (a.u.)	$\alpha_{\perp}$ (a.u.)
1.20	5.210	3.854
1.30	5.787	4.182
1.35	6.089	4.344
1.40	6.399	4.506
1.45	6.718	4.674
1.50	7.045	4.845
1.60	7.718	5.187

Table 4. The polarisability and polarisability gradients as given by the polynomial $\alpha(R)$ resulting from this and other calculations (given in a.u.)

	a	b	c	d	Ref.
$\alpha_{\parallel}$	6.399	6.295	1.615	−0.627	This work
	6.381	6.599	2.078	−0.347	Kołos and Wolniewicz [3]
	6.114	7.034	4.948	2.98	Ishiguro et al. [2]
	6.349				Wilkins and Taylor [17]
$\alpha_{\perp}$	4.508	3.306	0.313	0.067	This work
	4.578	3.223	0.202	−0.339	Kołos and Wolniewicz [3]
	4.447	4.043	2.803	−0.31	Ishiguro et al. [2]
	4.912				Wilkins and Taylor [17]

spectively at $R = R_0$. Results of this fit for $\alpha_{\parallel}$ and $\alpha_{\perp}$ are present in Table 4, where we have also listed corresponding results of Kołos and Wolniewicz (calculated for the range $1.20 \leq R \leq 1.60$), those of Ishiguro et al. and also the results of a good calculation based on the Hartree-Fock theory [17].

Electron Density Maps

To provide a more visual description of molecules in electric fields electron density maps were obtained for the H_2 molecule in the presence of both parallel and perpendicular fields. They are to be compared with that of the unperturbed molecule which is also presented.

To prepare a contour plot the spinless first order density matrix (normalized to 2) was evaluated and diagonalized resulting in the natural orbital expansion of the given wavefunction [11, 12]. Since the occupation number of the dominant natural orbital is two orders of magnitude greater than that of any other in the set, it is sufficient to plot twice the square of the dominant natural orbital. The magnitude of the field was taken to be 0.1 a.u. in each case, sufficiently large to show any distortion clearly, although somewhat too large for the effect to be due only to the polarisability.
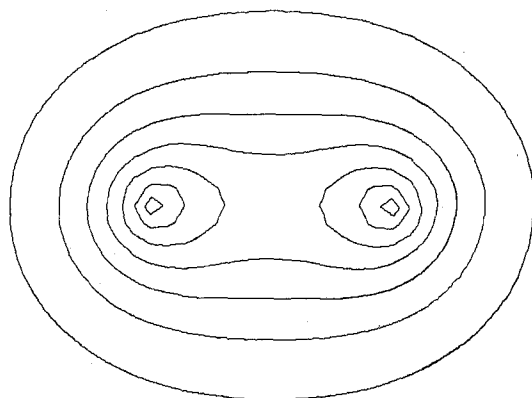
Fig. 1. Electron density map of the H_2 molecule. The contours correspond to densities of 0.05, 0.10, 0.15 ... 0.35. (The angular character of the contours near the nuclei is due to the relatively large separation (0.1 a.u.) of the grid points in the contouring routine)
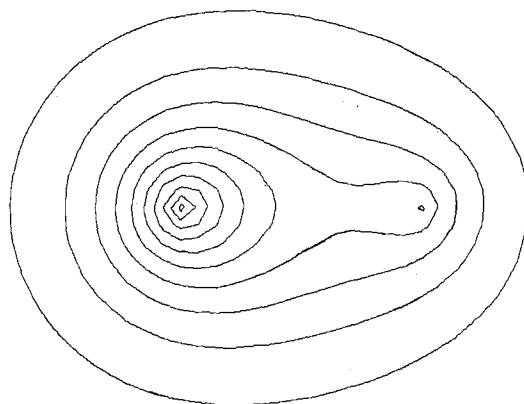

Fig. 2. Electron density map of the H_2 molecule in a uniform electric field of 0.1 a.u. parallel to the internuclear axis (directed from left to right). The contours correspond to densities of 0.05, 0.10, 0.15 ... 0.50

The electron density map of the unperturbed molecule is shown in Fig. 1, while Figs. 2 and 3 display the electron density in the presence of a field of 0.1 a.u. parallel to the molecular axis and the resulting electron density difference respectively. This strong field has a marked effect, causing a very noticeable polarisation. It is of interest to note that the electron density difference map is slightly asymmetrical, i.e. the build-up of charge on the left nucleus is more localized than the depletion of charge on the other. The analogous effect of a field of the same magnitude perpendicular to the internuclear axis, shown in Figs. 4 and 5, is much less marked. To understand this we must bear in mind that the change in charge density occurs over a larger region, resulting in an induced dipole moment of similar magnitude to the previous, i.e. parallel field, case.
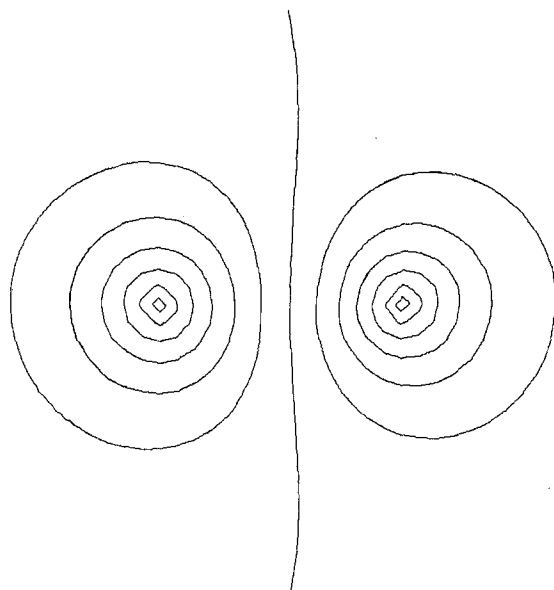
Fig. 3. Change in the electron density as a result of the parallel electric field of 0.1 a.u. The contours correspond to densities of 0.02, 0.04, 0.06 ... 0.12 left of the nodal plane (zero density) and to −0.02, −0.04, −0.06 ... −0.12 on the right
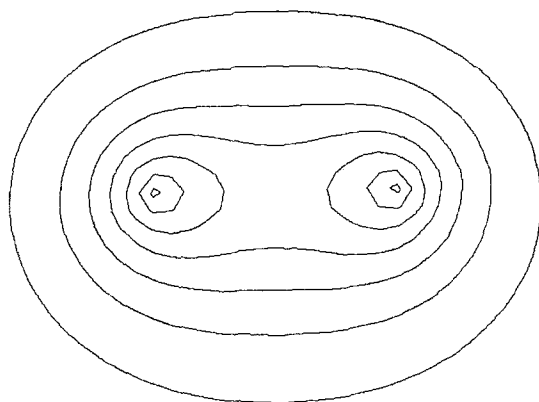

Fig. 4. The electron density in the presence of a uniform electric field of 0.1 a.u. perpendicular to the internuclear axis (directed upwards). The contours are 0.05, 0.10, 0.15 ... 0.35

Discussion

The results of our calculations, as summarized in Table 4, compare very favourably with the accurate results of Kołos and Wolniewicz [6], despite the much simpler nature of the wavefunctions used in our work. It is also very gratifying that not only the polarisabilities but their gradients too agree well with the accurate values of the above authors.
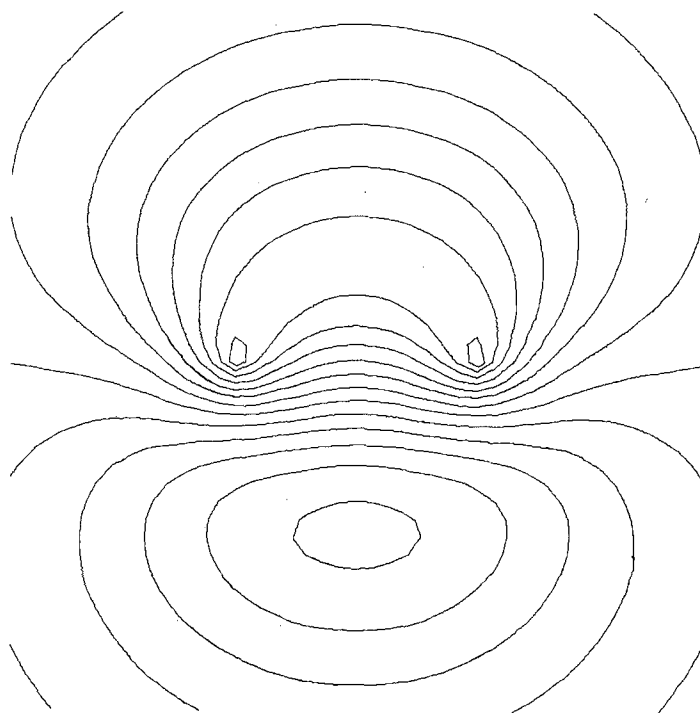
Fig. 5. Change in the electron density as a result of the perpendicular field of 0.1 a.u. The contours correspond to densities of 0.002, 0.004, 0.006, 0.008, 0.010; separated by a nodal plane from the contours -0.002, -0.004, -0.006 ... -0.014. The last set of contours encircle the nuclei

In the calculation of $\alpha_{\parallel}$ angular correlation in the total wavefunctions was neglected (the basis set contained only σ-type molecular orbitals) as it was expected to have little effect on $\alpha_{\parallel}$. This is borne out by our results as we believe the value of 6.399 to be very close to the limiting value for $\alpha_{\parallel}$, obtainable by the use of a complete σ basis. Some angular correlation is allowed for in the wavefunctions used in the calculation of $\alpha_{\perp}$ by including $\pi_{u_x}\pi_{u_x}$, $\pi_{g_x}\pi_{g_x}$ and $\sigma_u\pi_{g_x}$ type configurations in the perturbed wavefunctions. In all our calculations we found it important to use all the possible configurations, i.e. employ a full CI treatment, to ensure satisfactory convergence for $\alpha_{\parallel}$ or $\alpha_{\perp}$.

The results of Wilkins and Taylor [17], also given in Table 4, are certainly very good and their work shows the full potential of the Hartree-Fock method. Despite the warnings of Kolker and Karplus [3] $\alpha_{\parallel}$ was not calculated to be too high, although $\alpha_{\perp}$ was a little high. Their calculations did, however, allow for some electron correlation.

We feel that in the light of the present work and that of Wilkins and Taylor it should be possible to obtain fairly accurate polarisabilities and polarisability gradients for larger molecules too using MCSCF wavefunctions which are more accurate than the conventional HFSCF wavefunctions and little

more difficult to handle. We hope to carry out such calculations for molecules as complex as N_2 and CO with success.

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