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ABSTRACT

A summation technique is used to calculate the static dipole electric polarizabilities of molecular hydrogen. The technique requires a complete set of single-particle Hartree-Fock states. The occupied Hartree-Fock orbitals for molecular hydrogen are bound, and the complementary set of Hartree-Fock orbitals all lie in the continuum. Such a basis set permits one to evaluate the required sums by integrating over the excited states. The uncoupled Hartree-Fock model is used to calculate the zero-order terms of the components of the polarizability tensor. The first-order corrections to the components of the polarizability tensor are calculated using double perturbation theory. At the equilibrium internuclear separation, $R = 1.4\ a_0$, the static parallel dipole polarizability $\alpha^{\parallel}$ and static perpendicular polarizability $\alpha^{\perp}$ are 0.941 $Å^3$ and 0.728 $Å^3$, respectively, which compare favorably with the values 0.944 $Å^3$ and 0.677 $Å^3$ calculated by Kolos and Wolniewicz using a variation-perturbation method. The results are also in satisfactory agreement with the experimental values.

AD674071

Polarizability of Molecular Hydrogen

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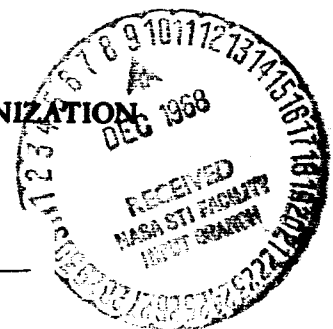University of Southern California

July 1968

Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION

N69-12099

FACILITY FORM 602

(ACCESSION NUMBER) _____ (THRU)
___17___ ___/___
(PAGES) (CODE)
CR-97879 ___24___
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

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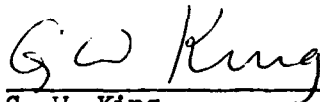Los Angeles, California

FOREWORD

This report is published by the Aerospace Corporation, El Segundo, California, under Air Force Contract F04695-67-C-0158.

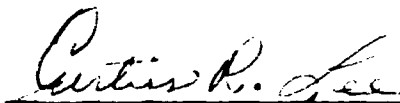The research documented in this report was carried out from March to September 1967 and was supported, in part, under NASA Contract NSG-616. This report was submitted on 25 July 1968 to Lieutenant Curtiss R. Lee, SMTTM, for review and approval.

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

ABSTRACT

A summation technique is used to calculate the static dipole electric polarizabilities of molecular hydrogen. The technique requires a complete set of single-particle Hartree-Fock states. The occupied Hartree-Fock orbitals for molecular hydrogen are bound, and the complementary set of Hartree-Fock orbitals all lie in the continuum. Such a basis set permits one to evaluate the required sums by integrating over the excited states. The uncoupled Hartree-Fock model is used to calculate the zero-order terms of the components of the polarizability tensor. The first-order corrections to the components of the polarizability tensor are calculated using double perturbation theory. At the equilibrium internuclear separation, $R = 1.4\ a_0$, the static parallel dipole polarizability $\alpha^{\parallel}$ and static perpendicular polarizability $\alpha^{\perp}$ are $0.941\ \mathring{A}^3$ and $0.728\ \mathring{A}^3$, respectively, which compare favorably with the values $0.944\ \mathring{A}^3$ and $0.677\ \mathring{A}^3$ calculated by Kolos and Wolniewicz using a variation-perturbation method. The results are also in satisfactory agreement with the experimental values.

CONTENTS

TABLE

I. INTRODUCTION

Several authors (Refs. 1-4) have used various variation-perturbation tech-
niques to evaluate the principal values of the components of the polarizability
tensor of molecular hydrogen. The most accurate calculations reported are those
presented recently by Kolos and Wolniewicz (Ref. 4). Their zero-order wave-
functions included electron correlation, which is known to have a substantial
effect on atomic and molecular properties (Ref. 5). The polarizabilities of
H_2 were overestimated by the Kolker and Karplus (Ref. 3) technique. Their zero-
order wavefunctions did not include electron correlation. The effects of corre-
lation on polarizability can be calculated using double perturbation theory even
though the exact wavefunction of the molecule is not known.

There are other approximate methods for calculating the polarizability of
a many-electron system (Ref. 6). These include the coupled and uncoupled Hartree-
Fock methods. The coupled Hartree-Fock method, which is considered the more
accurate of the methods, requires many self-consistency conditions on the per-
turbed one-electron orbitals. The resulting perturbation equations for the one-
electron orbitals are coupled. One has to solve N coupled equations for an N-
body problem, and herein lies the difficulty of the coupled Hartree-Fock method.
In a recent paper Musher (Ref. 7) shows that there is no advantage in performing
the difficult calculations required in using the coupled Hartree-Fock method.
One can obtain second-order properties as accurate as the coupled Hartree-Fock
method by evaluating the first two terms of a straightforward perturbation theory.
The labor involved in the former is considerably greater than that involved in
the latter. Hirschfelder, Byers Brown, and Epstein (Ref. 8) have derived
equations for the first-order-perturbation-theory corrections for first- and
second-order properties to the uncoupled-perturbation-theory method. In applying
these equations to atoms and molecules, it is necessary to know the spectrum of
the unperturbed Hamiltonian. We use the Hartree-Fock model for the unperturbed
problem. Kelley and Taylor (Ref. 9) have shown that when the unperturbed problem
is the Hartree-Fock model it is not necessary to resort to a variation method to
solve the perturbation equations. The first- and second-order perturbed

wavefunctions can be determined by an expansion in the complete set of excited states of the Hartree-Fock Hamiltonian. The interesting feature for closed-shell atomic and molecular systems is that the excited states all lie in the continuum. This basis set allows one to evaluate the infinite summations of perturbation theory by summing over a small number of bound states and integrating over the excited states. Wilkins (Ref. 10) has shown that this basis set for molecular hydrogen contains the Hartree-Fock orbitals of the ground state, and all other orbitals are in the continuum. This complete set of single-particle Hartree-Fock states has been used to calculate some first- and second-order properties of molecular hydrogen. These calculations did not consider the effect of intramolecular electron correlation on second-order properties such as polarizabilities of a molecule or the van der Waal's coefficient for the interaction between two molecules. It is the purpose of this paper to use the basis set for molecular hydrogen to calculate the components of the polarizability tensor of molecular hydrogen to first-order in correlation employing double perturbation theory. In Section II we outline the method proposed by Hirschfelder, Byers Brown, and Epstein (Ref. 8) to calculate a second-order property to first-order in correlation effects using double perturbation theory. In Section III the results of Section II are used to develop equations for the components of the polarizability tensor for molecular hydrogen using the basis set. In Section IV numerical results, as well as their discussion, are given.

The calculations presented in this paper are the first on a molecule in which a complete set of Hartree-Fock states are used to calculate both the weak interaction and electron correlation simultaneously. The components of the polarizability tensor of molecular hydrogen have not been calculated by the coupled Hartree-Fock method. Nevertheless, our results are in very good agreement with the experimental results and with the more accurate results obtained by Kolos and Wolniewicz (Ref. 4) using a variation-perturbation method in which the zero-order wavefunctions include electron correlation.

II. DOUBLE PERTURBATION THEORY

Consider a system subjected to two perturbations λV and μW. In this paper λV is the intramolecular electron correlation, and μW is the external field. The external-field perturbation μW is much simpler than the electron-correlation perturbation λV. We use, therefore, double perturbation theory to express the first-order correction of the electron-correlation perturbation in terms of the more easily calculated second-order correction of the external-field perturbation. The derivation of the essential equations follows that of Hirschfelder, Byers Brown, and Epstein (Ref. 8). The Hamiltonian of the perturbed system can be written as

$$H = H_0 + \mu W + \lambda V , \tag{1}$$

where H_0 is the unperturbed Hamiltonian. Double perturbation theory assumes that the wavefunction Φ and energy E for the perturbed state can be expanded in a double power series in λ and μ,

$$\Phi = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda^n \mu^m \psi^{(n,m)} , \tag{2}$$

$$E = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda^n \mu^m \epsilon^{(n,m)} . \tag{3}$$

One obtains for the mixed perturbation equations

$$H_0 \psi^{(n,m)} + V\psi^{(n-1,m)} + W\psi^{(n,m-1)} = \sum_{j=0}^{n} \sum_{k=0}^{m} \epsilon^{(j,k)} \psi^{(n-j,m-k)} . \tag{4}$$

The perturbed function Φ must be normalized to unity for all values of λ and μ, which implies that the double perturbed wavefunctions $\psi^{(j,k)}$ must satisfy

$$\sum_{j=0}^{n} \sum_{k=0}^{m} \langle \psi^{(j,k)}, \psi^{(n-j,m-k)} \rangle = \delta_{n0} \delta_{m0}, \qquad n,m = 0,1,2 \cdots . \tag{5}$$

The double perturbation energies $\epsilon^{(n,m)}$ can be obtained by multiplying Eq. (4) by the approximate Hartree-Fock wavefunction ψ and integrating over all space to obtain

$$\epsilon^{(n,m)} = \langle \psi, V\psi^{(n-1,m)} \rangle + \langle \psi, W\psi^{(n,m-1)} \rangle$$

$$-\sum_{j=0}^{n} \sum_{k=0}^{m} \epsilon^{(j,k)} \left[(1 - \delta_{j,0})(\delta_{k,0} - \delta_{j,n})\delta_{k,m} \right] \langle \psi, \psi^{(n-j,m-k)} \rangle . \tag{6}$$

The second-order perturbation energy can be expressed in terms of the double perturbation energies

$$E^{(2)} = \sum_{n=0}^{\infty} \lambda^n \epsilon^{(n,2)} . \tag{7}$$

Dalgarno's interchange theorem (Ref. 8) allows one to express the double perturbation energies $\epsilon^{(1,m)}$ in terms of the W-perturbed functions $\psi^{(0,m)}$,

$$\epsilon^{(1,m)} = \sum_{k=0}^{m} \langle \psi^{(0,m-k)}, V\psi^{(0,k)} \rangle . \tag{8}$$

By applying Eq. (7) and using Eq. (8) for $\epsilon^{(1,2)}$ the second-order property $\langle Q \rangle$ can be expressed as

$$\langle Q \rangle = \langle Q \rangle_0 + \lambda \langle Q \rangle_1 + \cdots , \tag{9}$$

where

$$\langle Q \rangle_0 = \langle \psi^{(0,1)}, W\psi \rangle , \tag{10}$$

$$\langle Q \rangle_1 = \langle \psi^{(0,2)}, V\psi \rangle + \langle \psi, V\psi^{(0,2)} \rangle + \langle \psi^{(0,1)}, V\psi^{(0,1)} \rangle , \tag{11}$$

$\langle Q \rangle_0$ is the uncoupled Hartree-Fock approximations to $\langle Q \rangle$, and $\langle Q \rangle_1$ is the first-order correction to the ·ncoupled Hartree-Fock approximation. The perturbation functions $\psi^{(0,1)}$ and $\psi^{(0,2)}$ can be expanded in terms of the unperturbed functions ψ_k. One obtains by using Eqs. (10) and (11) the following expressions:

$$\langle Q \rangle_0 = 2 \sum_k{}' \left[W_{qk}^{(0)} W_{kq}^{(0)} / (\epsilon_q - \epsilon_k) \right] , \tag{12}$$

$$\langle Q \rangle_1 = 2 \sum_k{}' \sum_j{}' \frac{\left(V_{qk}^{(0)} W_{kq}^{(0)} W_{jq}^{(0)} + W_{qk}^{(0)} V_{kj}^{(0)} W_{jq}^{(0)} + W_{qk}^{(0)} W_{kj}^{(0)} V_{jq}^{(0)} \right)}{\left(\epsilon_q - \epsilon_k \right)\left(\epsilon_q - \epsilon_j \right)} . \tag{13}$$

The first-order corrections $\langle Q \rangle_1$ to the second-order property $\langle Q \rangle$ due to the correlation perturbation is effected through the matrix elements $V_{kj}^{(0)}$ in the terms of order λ [see Eq. (9)]. The sums in Eqs. (12) and (13) must include integration over the continuum, and the primes imply that states with energy ϵ_q are omitted. In Eqs. (12) and (13)

$$W_{kj}^{(0)} = \langle \psi_k, W\psi_j \rangle - \delta_{kj} \langle \psi_q, W\psi_q \rangle \tag{14}$$

and

$$V_{kj}^{(0)} = \langle \psi_k, V\psi_j \rangle - \delta_{kj} \langle \psi_q, V\psi_q \rangle . \tag{15}$$

Equations (14) and (15) are calculated for all values of k and j except for both j and k equal 2. In Section III we use Eq. (13) to derive the equations for the electron correlations to the components of the electric dipole polarizability tensor of molecular hydrogen.

III. APPLICATION TO DIPOLE POLARIZABILITY

In this section we apply Eq. (13) to calculate the parallel and perpendicular electric dipole polarizabilities of molecular hydrogen. The operator W for the polarizability tensor is the electric dipole moment vector $\bar{\mu}$. The electron-correlation correction to the polarizability $\alpha_q^{(1)}$ is obtained by replacing W in Eq. (13) by $\bar{\mu}$,

$$\langle Q \rangle_1 = \alpha_q^{(1)} = 2 \sum_k \sum_j{}' \frac{\left(\mu_{qk}^{(0)} v_{kj}^{(0)} \mu_{jq}^{(0)} + 2\mu_{qk}^{(0)} \mu_{kj}^{(0)} v_{jq}^{(0)} \right)}{\left(\epsilon_q - \epsilon_k \right)\left(\epsilon_q - \epsilon_j \right)} , \tag{16}$$

where

$$\mu_{kj}^{(0)} = \langle \psi_k, \bar{\mu}\psi_j \rangle - \delta_{kj} \langle \psi_q, \bar{\mu}\psi_q \rangle . \tag{17}$$

The parallel component of the polarizability is obtained from Eq. (16) by using for the vector $\bar{\mu}$ the z component of $\bar{\mu}$. The perpendicular component of the polarizability requires the x or the y component of the dipole moment vector $\bar{\mu}$. Wilkins (Ref. 10) has shown that all the unoccupied Hartree-Fock states lie in the continuum. It follows that the sums of Eq. (16) can be replaced by an integration over the continuum states. By replacing ϵ_k by $\frac{1}{2} k^2$ and ϵ_j by $\frac{1}{2} (k')^2$ one obtains for the first-order correction to polarizability that

$$\langle Q \rangle_1 = \alpha_q^{(1)} = 2 \int_0^\infty \int_0^\infty \frac{dk \, dk' \left[\mu_{qk}^{(0)} v_{kk'}^{(0)} \mu_{kq}^{(0)} + 2\mu_{qk}^{(0)} \mu_{kk''}^{(0)} v_{k''q}^{(0)} \right]}{\left(\epsilon_q - \frac{1}{2} k^2 \right)\left[\epsilon_q - \frac{1}{2}(k')^2 \right]} . \tag{18}$$

The ground-state eigenfunction ψ_q for molecular hydrogen is

$$\psi_q = 1\sigma_g(1) \, 1\sigma_g(2) \left[\alpha(1)\beta(2) - \beta(1)\alpha(2) \right] \big/ \sqrt{2} , \tag{19}$$

where α and β are the spin components and the one-electron molecular orbital $1\sigma_g(\bar{r})$ is defined as

$$1\sigma_g(\bar{r}) = (4\pi)^{-1/2} \sum_{n=0}^{\infty} f_{2n}(r)\, P_{2n}^0(\mu) ,$$ (20)

where $f_{2n}(r)$ is the radial wavefunction obtained from a numerical solution of the Hartree-Fock equation for molecular hydrogen using an expansion about a single center (Ref. 10), $P_{2n}^0(\mu)$ the associated Legendre polynomial, and $\mu = \cos\theta$. The total wavefunctions for the excited states required for the parallel components of the polarizability tensor can be written as

$$\psi_k = \frac{1}{2}\Big[1\sigma_g(1)\, k\sigma_u(2) + k\sigma_u(1)\, 1\sigma_g(2)\Big]\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big]$$ (21)

and

$$\psi_{k''} = \frac{1}{2}\Big[k\sigma_u(1)\, k'\sigma_u(2) + k\sigma_u(2)\, k'\sigma_u(1)\Big]\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big] ,$$ (22)

and the excited states required for the perpendicular component of the polarizability tensor can be written as

$$\psi_k = \frac{1}{2}\Big[1\sigma_g(1)\, k\pi_u^{+1}(2) + k\pi_u^{+1}(1)\, 1\sigma_g(2)\Big]\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big]$$ (23)

and

$$\psi_{k''} = \frac{1}{2}\Big[k\pi_u^{+1}(1)\, k'\pi_u^{-1}(2) + k\pi_u^{+1}(2)\, k\pi_u^{-1}(1)\Big]\Big[\alpha(1)\beta(2) - \beta(1)\alpha(2)\Big] .$$ (24)

The excited one-electron molecular Hartree-Fock orbitals are defined as

$$k\sigma_u(1) = (4\pi)^{-1/2}\left(\frac{2}{\pi}\right)^{1/2} \sum_{s=0}^{\infty} f_{k,2s+1}^0(r_1) P_{2s+1}^0(\mu_1)$$ (25)

and

$$k\pi_u^{\pm}(1) = (4\pi)^{-1/2}\left(\frac{2}{\pi}\right)^{1/2}\sum_{s=0}^{\infty} f_{k,2s+1}^{(1)}(r_1)\, P_{2s+1}^{(1)}(\mu_1)\, \exp(\pm\, i\phi_1)\, , \qquad (26)$$

where the subscript k on the radial functions f refers to the continuum energy and the superscript refers to the values of the component of angular momentum along the internuclear axis. The factor $(2/\pi)^{1/2}$ gives the continuum functions the proper normalization. The parallel and perpendicular components of the polarizability tensor are obtained by substituting Eq. (19) and Eqs. (21) and (22) or Eqs. (23) and (24), respectively, into Eq. (18) and making use of the fact that V in Eq. (18) is the electron-electron repulsion minus the Hartree-Fock potential,

$$V = (r_{12})^{-1} - \int \frac{|\psi_q(r_1)|^2\, d\vec{r}_1}{r_{12}} - \int \frac{|\psi_q(r_2)|^2\, d\vec{r}_2}{r_{12}}\, . \qquad (27)$$

IV. RESULTS AND DISCUSSION

The computations were carried out for $R = 1.40$ au on the CDC 6600 computer at the Aerospace Corporation. The most time-consuming part of the calculations is the evaluation of the matrix elements $V_{k,k'}$ of the infinite matrix V. If N identical values are chosen for k and k', then the matrix V has N^2 elements. However, one needs only calculate $\frac{1}{2} N(N + 1)$ matrix elements instead of N^2 matrix elements, because the matrix V is symmetrical. Since the matrix elements $\mu_{q,k}^{(0)}$ decrease rapidly toward zero with increasing k values, one can evaluate the required integrals by integration over a small range of values for k and k'. The continuum functions are evaluated at 36 values of k. The continuum functions along with the bound functions are used to evaluate 36 matrix elements $\mu_{q,k}^{(0)}$ and 666 matrix elements $V_{k,k'}$. The double integration indicated in Eq. (18) was accomplished using Weddle's rule to put the best polynomial through the calculated points. In Table I we list our results for the components of the polarizability tensor for molecular hydrogen at zero frequency. Table I indicates that the components of the polarizability tensor are in error by about 25% if the electron-correlation effects are not included. The results in Table I for the components of the polarizability tensor compare favorably with the experimental values (Ref. 11) of 0.728 $Å^3$ for $\alpha^\perp$ and 0.934 $Å^3$ for $\alpha^\parallel$. Our results are in very good agreement with Kolos and Wolniewicz (Ref. 4) theoretical values at $R = 1.4$ a_0 of 0.677 $Å^3$ for $\alpha^\perp$ and 0.944 $Å^3$ for $\alpha^\parallel$.

The results presented in this paper constitute the first attempt at an accurate calculation of the polarizability tensor of a diatomic molecule starting with the uncoupled Hartree-Fock approximation. The inclusion of the electron-correlation correction gives results that are as accurate as those obtained from solving the coupled Hartree-Fock perturbation problem. The method described in this paper could easily be extended to larger Hartree-Fock systems. It can be used also to calculate coefficients of higher multipole interactions. The method has the advantage that the perturbed orbitals are not required to satisfy any

self-consistency conditions. Therefore, it is our opinion that the double
perturbation technique is of comparable accuracy and has many advantages over
other methods that have been proposed.

Table I. Static Polarizabilities in $\overset{o}{A}{}^3$

	$\alpha^{\parallel}$	$\alpha^{\perp}$
$\alpha_q^{(0)} = \langle Q \rangle_0$	0.7108	0.4849
$\alpha_q^{(1)} = \langle Q \rangle_1$	0.2300	0.2430
α	0.9408	0.7279

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DOCUMENT CONTROL DATA · R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*	2a REPORT SECURITY CLASSIFICATION
Aerospace Corporation El Segundo, California	Unclassified
	2b GROUP

3 REPORT TITLE

POLARIZABILITY OF MOLECULAR HYDROGEN

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5 AUTHOR(S) *(Last name, first name, initial)*

Wilkins, Roger L., and Taylor, Howard S.

6 REPORT DATE	7a TOTAL NO OF PAGES	7b. NO. OF REFS
July 1968	15	14

8a CONTRACT OR GRANT NO.	9a ORIGINATOR'S REPORT NUMBER(S)
F04695-67-C-0158	TR-0158(3240-20)-20
b. PROJECT NO	
c	9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d	SAMSO-TR-68-327

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11 SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Space and Missile Systems Organization Air Force Systems Command Los Angeles, California

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14. KEY WORDS

Hartree-Fock
Molecular Hydrogen
Polarizability

Abstract (Continued)