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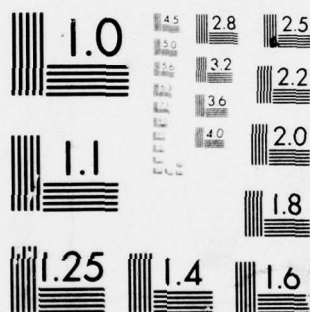
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M. Krauss,
F. H. Mies,
D. B. Neumann
P. S. Julianne

Quantum Chemistry Group
Physical Chemistry Division
National Bureau of Standards
Washington, D.C. 20234

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The coupled Hartree-Fock(CHF), method was applied to neutral atoms of the first row. The method was applied with and without the inclusion of electron correlation. When electron correlation was included vis the coupled multiconfigurational self-consistent field, (CMCSCF), method, which is a straightforward extension of the CHF method it was found that correlation effects account for less than 10 percent of the polarizability. Further investigations regarding the basis set via including more or less flexibility showed that extensions of basis set size affected the polarizabilities by less		

1. Introduction

The polarizabilities of ionic states of atoms are quantities of importance in the determination of long range forces between atoms where either excited states are present which are ionic in character or which exhibit a large degree of charge transfer.¹ The electric dipole polarizability represents the major interaction of a static electric field with an atom or ion. A considerable number of methods have been proposed and applied to the calculation of atomic polarizabilities. These range from the solution of the perturbation equations describing the influence of the field on the atoms to very complete variational methods with large numbers of configurations.

The perturbation equations arising when atomic exchange effects are neglected have been solved by variational techniques for small atoms by Kirkwood, Buckingham and others.² Dalgarno and Parkinson³ achieved moderate accuracy for first row atoms by solving for the first order perturbed orbitals in the presence of exchange. More recently calculations of atomic polarizabilities have been performed using the coupled Hartree-Fock, (CHF), method,⁴⁻⁷ the coupled Hartree-Fock perturbation, (CHFP), method,⁸⁻¹⁰ the double perturbation theory,¹¹⁻¹³ and the many-body perturbation theory.¹⁴⁻¹⁶ In these techniques the Hartree or Hartree-Fock wave function is used as a zeroth-order approximation from which the first-order perturbed function for the atom in the field is obtained.³ In the CHF method the HF equations for the atom are variationally solved in the presence of a finite field. In the

CHFP method the polarizability is expressed as a function of the change in the second order energy of the atom,³ while in the CHF method the variationally determined wave function for the system in the presence of the field is used to determine the induced dipole moment as a function of the field. The polarizability may then be expressed as the limit of the ratio of the induced dipole moment to the field as the field goes to zero. If sufficiently accurate wave functions are used the CHF and CHFP methods are equivalent.

In previous work by this group^{17,18} the CHF method was applied to neutral atoms of the first row. The method was applied with and without the inclusion of electron correlation. When electron correlation was included via the coupled multi-configurational self-consistent field, (CMCSCF), method, which is a straightforward extension of the CHF method it was found that correlation effects account for less than 10% of the polarizability.^{17,19} Further investigations regarding the basis set via including more or less flexibility showed that extensions of basis set size affected the polarizabilities by less than 5%.¹⁸

In the present work a simple ad hoc scheme for choosing basis sets of ions and atoms was sought which when used with a CHF calculation, without the inclusion of correlation effects, would give polarizabilities for ions to 10-20% accuracy. The accuracy will be poorest for particular atomic states where correlation effects are substantial.²⁰

In addition to the work on the polarizabilities, we have begun to prepare the recent work on N_2 for publication. The abstract for the paper "The $5\Pi_u - 5\Sigma_g^+$ Transition in N_2 " is included.

II. Review of the Method

In the previous work of our group by Billingsley, Krauss and Stevens^{17,18} a CHF method was used in which the atom was subjected to static field due to a unit charge at a relatively large distance 10-20 a.u. from the atom. The wave function in the presence of the charge was computed variationally. From the dipole moment induced by the charge the polarizability was determined. As the field is not uniform the dipole is induced not by the field alone but also by gradients and higher derivatives of the field.²¹ In the present work, in order to avoid any ambiguities introduced by the nonuniformity of the field the technique of Cohen and Roothaan was applied.^{4,5} In their application of the CHF technique the atom is subjected to a uniform field, $\vec{F}$. The total Hamiltonian for the system is:

$$\underline{H} = \underline{H}_0 + F h \quad (1)$$

where $h = -\sum_{i=1}^N \frac{\vec{F} \cdot \vec{r}_i}{F}$ and $\underline{H}_0$ is the Hamiltonian for the unperturbed ion. The field used is directed along the z-axis of the system. This destroys the spherical symmetry bringing the atom to $C_{\infty v}$ symmetry. For the $1S$ state of F^- this produces a $1\Sigma^+$ state. It is for this state that the polarizability is determined. The wave function can be written:

$$\psi = \psi_0 + F\psi_1 + F^2\psi_2 + \dots \quad (2)$$

where $F = |\vec{F}|$, ψ_0 is the unperturbed HF wave function for the N-electron ion. If ψ_0 were the exact wave function of the unperturbed system then

$$(H_0 - E_0)\psi_0 = 0 \quad (3)$$

and ψ_1 is the solution of

$$(H_0 - E_0)\psi_1 + h\psi_0 = 0 \quad (4)$$

In such a perturbation approach the static electric dipole polarizability becomes:

$$\alpha = -2\langle\psi_0|h|\psi_1\rangle \quad (5)$$

In the present CHF method the wave function for the system is determined for particular values of the field along the z-axis and one can calculate the dipole moment induced by the field:

$$\mu(F) = \langle\psi|h|\psi\rangle \quad (6)$$

The polarizability is then found by the classical definition:

$$\alpha = \lim_{F \rightarrow 0} [\mu(F)/F] \quad (7)$$

when higher terms are included then the induced moment may be written for the atom or ion as:

$$\mu(F) = \alpha F + \frac{1}{6} \gamma F^3 + \dots \quad (8)$$

where γ is known as the static electric dipole hyperpolarizability.

A second method of determining the polarizability is from the change in the energy of the system due to the field. The energy may be written:

$$\begin{aligned} E(F) &= \langle\psi|H_0 + Fh|\psi\rangle \\ &= \langle\psi_0| & + F^2\{2\langle\psi_0|h|\psi_1\rangle + \langle\psi_1|H_0|\psi_1\rangle - 2\langle\psi_0|H_0|\psi_2\rangle\} \\ &\quad + 2F^4\{\langle\psi_0|h|\psi_3\rangle + \langle\psi_1|h|\psi_2\rangle + \langle\psi_1|H_0|\psi_3\rangle \\ &\quad + \frac{1}{2}\langle\psi_2|H_0|\psi_2\rangle + \langle\psi_0|H_0|\psi_4\rangle\} \end{aligned} \quad (9)$$

Terms proportional to odd powers of F are absent due to parity considerations. Thus by using the relationship for the exact first-order wave function (4) in the second term of (9), and

and omitting the probably small term $\langle \psi_0 | H_0 | \psi_2 \rangle$, one obtains:

$$\begin{aligned} \Delta E(F) &= E(F) - E(F=0) \\ &= F^2 \langle \psi_0 | h | \psi_1 \rangle + O(F^4) \end{aligned} \quad (10)$$

which when coupled with (5) gives

$$\alpha(F) = -2\Delta E(F)/F^2 \quad (11)$$

thus:

$$\alpha = \lim_{F \rightarrow 0} \{-2\Delta E(F)/F^2\} \quad (12)$$

In the present work both eqs. (12) and (7) were applied. It was found that these two different definitions of α do not give precisely the same result. This is basically due to the fact that the wave functions ψ_0, ψ_1 used in the calculation are not exact as is required for the two definitions to be equivalent. They have been shown also to be equivalent for HF wave functions by Cohen^{5,22} with the further proviso that Brillouins' theorem holds for ψ_0 . Insofar as the wave functions, ψ_0 , used in this work are not exact solutions to the Hartree-Fock equations nor does Brillouins' theorem hold once spherical symmetry is broken, it is not surprising that the equivalence between the two definitions is found not to hold exactly.

In addition to the polarizability, the hyperpolarizability may be determined by fitting the induced moment (8) or from the initial slope of $\mu(F)/F$. In a similar manner to (5) the hyperpolarizability can be written by omitting probably small terms:

$$\gamma = 12\{\langle \psi_1 | h | \psi_2 \rangle + \langle \psi_0 | h | \psi_3 \rangle\} \quad (13)$$

III. Computational Methods

The calculations reported herein were performed with the BISON-MC system of programs of Wahl, Das, et al.²³ The BISON-MC programs determine variationally the wave function which is expressed as a linear combination of Slater determinants. In the present case a single determinant was used as correlation effects were ignored. The atomic orbitals of the Slater determinant are in turn expressed as linear combinations of atomic centered Slater type orbitals, STO's. The wave functions were generated using the Hamiltonian (1) with fields varying from 0.0020 to 0.0060 a.u. The calculations were performed in $C_{\infty v}$ symmetry. Calculations with the field set to zero were done. These gave slightly lower total energies than the calculations done in spherical symmetry. In the present case of a 1S atom this lowering was quite small. This is in contrast to atomic calculations done in $C_{\infty v}$ symmetry where the atom was in a degenerate state¹⁷ where larger energy lowerings occur when the spherical symmetry is broken.

In the present CHF method the polarizability is calculated using a basis set for the atom consisting of two parts. The first part is the Hartree-Fock basis for the atom. The Hartree-Fock basis set of Clementi for $F^-(^1S)$ was used. The second part of the basis set consists of the polarization functions. Sitter and Hurst have reported rules for choosing the principal quantum number and spherical harmonic portions of the polarization orbitals.⁷ There remains the choice of the exponents of these polarization functions. They may be chosen by a method described by Billingsley

and Krauss¹⁷ in which the functional:

$$\epsilon_2 = \langle u_i^{(1)} | \bar{H}_i^0 - \epsilon_i^0 | u_i^{(1)} \rangle + 2 \langle u_i^{(1)} | \bar{h}_i | u_i^{(0)} \rangle \quad (14)$$

is minimized. Here $u_i^{(0)}$ is the Hartree-Fock orbital and $u_i^{(1)}$ is the polarizational orbital.

$$\begin{aligned} \bar{H}_i^0 &= -\frac{1}{2} \nabla_i^2 + V_i(r_i) \\ h &= \sum_{i=1}^N h_i; \quad h_i = \vec{F} \cdot \vec{r}_i / F \end{aligned} \quad (15)$$

and ϵ_i^0 is the orbital energy of the i -th orbital. Though this method has a firm theoretical base it is difficult to apply as the potential V_i is a two electron potential; hence Billingsley and Krauss simplified by using an effective potential:

$$V_i(r_i) = \frac{n^*(n^*-1)}{r_i^2} - \frac{\zeta_i^{(0)}}{r_i} \quad (16)$$

due to Slater and Zener.²⁴ Still in order to apply their method of choosing exponents for the polarization functions a further simplification was made. They chose to represent $u_i^{(0)}$ and $u_i^{(1)}$ by single Slater basis functions.

In the present work a similar although completely ad hoc method was used to choose polarization functions. The integral

$$\langle u_i^{(1)} | \bar{h}_i | u_i^{(0)} \rangle$$

was maximized, and $u_i^{(0)}$ and $u_i^{(1)}$ were represented by single Slater orbitals. This gave rise to a set of rules to be used in combination with those of Sitter and Hurst.⁷ Thus when basis functions are to be chosen to allow for polarization of a Hartree-Fock orbital whose most significant function is $\chi_{nl}^{(0)}(\zeta^{(0)}, \vec{r})$ choose polarization

functions $\chi_{n'l}^{(1)}, (\zeta^{(1)}, \vec{r})$ by the rules:

$$\begin{aligned} 1s(\zeta^{(0)}) \text{ polarize with } 2p(\zeta^{(1)} &= \zeta^{(0)}) \\ &\text{and } 3p(\zeta^{(1)} = 7\zeta^{(0)}/5) \\ 2s(\zeta^{(0)}) \text{ polarize with } 2p(\zeta^{(1)} &= 5\zeta^{(0)}/7) \\ &\text{and } 3p(\zeta^{(1)} = \zeta^{(0)}) \\ &\text{and } 4p(\zeta^{(1)} = 9\zeta^{(0)}/7) \\ 2p(\zeta^{(0)}) \text{ polarize with } 1s(\zeta^{(1)} &= 3\zeta^{(0)}/7) \\ &\text{and } 2s(\zeta^{(1)} = 5\zeta^{(0)}/7) \\ &\text{and } 3s(\zeta^{(1)} = \zeta^{(0)}) \\ &\text{and } 4s(\zeta^{(1)} = 9\zeta^{(0)}/7) \\ &\text{and } 3d(\zeta^{(1)} = \zeta^{(0)}) \\ &\text{and } 4d(\zeta^{(1)} = 9\zeta^{(0)}/7) \end{aligned}$$

Should $u_i^{(0)}$ have more than one significant basis function then choose polarization functions for each of them. Omit any polarization functions which strongly overlap the space of functions used to describe ψ_0 to prevent over completeness of the basis set.

In using the Clementi Hartree-Fock basis sets for an atom²⁶ it frequently occurs that there are three or more functions which have large atomic orbital coefficients. In such a case it is necessary to pick the polarization functions using the above rules, but based on the exponents of a smaller optimized atomic basis set. This is easily done (even when the exponents of the smaller basis set are not known but the exponents of a very small basis set are known) by an extrapolation technique used originally by Hornback²⁵ with gaussians. The logarithm of the exponents is plotted versus the size of the basis set and extrapolation to smaller basis sets

is performed. In figure 1 the exponents of the basis functions for the 2p orbital of F^- are plotted for several basis set sizes. It is easily seen that interpolation or extrapolation should be quite accurate.

Using the above ad hoc rules the polarization functions for F^- were chosen. The full basis set is given in Table I as Set I. These ad hoc rules should be sufficient to compute polarizabilities to within 10 to 20% accuracy for many ions. To further test the method of choosing the basis set a second larger basis set was chosen in a manner similar to that of Billingsley and Krauss for Carbon.¹⁷ This basis is given in Table I as Set II.

IV. Results for $F^-(^1S)$

In Table II the change in the energy, $\Delta E(F)$, relative to $E(F=0)$ is given as a function of the field for basis set I. The energy for the spherically symmetric $F^-(^1S)$ system is given by Clementi²⁶ as -99.459363. Using basis set I in the absence of a field we obtain a lowering of the energy by only 5.4822×10^{-6} a.u. This small change is due to the inclusion of the 2s polarization function. In Table II the induced dipole moment as a function of the field is also presented. Due to the use of a single component of the field F_z rather than three equal field components $F_x = F_y = F_z$ a slight quadrupole moment is induced into the system. This moment $-\frac{1}{2} \langle \psi | \sum_i (3z_i^2 - r_i^2) | \psi \rangle$ is given in Table II as a function of the field as is also the relative value, ΔX , of the expectation value of $\sum_i^N (x_i^2 + y_i^2)$. The polarizability as a function of the field is given by both the expressions (7) and (11). These values are plotted in Fig. 2. From Table II it can also be seen that the small quadrupole moment induced in the ion is directly proportional to F^2 with a slight higher order effect present. Thus from Table II it can be seen that both ΔX and the magnitude of the quadrupole are increasing with the field, but the overall changes are very small. From the plot of the polarizability as a function of the field in Fig. 2, it can be seen that basis set I gives a static dipole polarizability of 9.398 a.u. using the induced dipole moment expression and a slightly larger value 9.402 a.u. using the energy expression.

In Table III the results are given for the calculation using basis set II. The polarizability via expressions (7) and (11) is plotted for basis set II in Fig. 2. The dipole moment expression, (7), gives a polarizability of 8.804 a.u. while the energy expression, (11), gives a polarizability slightly larger 8.810 a.u.

The plots of polarizability versus the square of the field, as shown in Fig. 2, show that the limiting value of α is only slightly different when expressions (7) or (11) are used. Second, the plot shows especially for basis set II a certain amount of scatter when the induced dipole moment is used via expression (7) to determine the polarizability. There seems to be considerably less scatter when the second order energy is used via expression (11) for the polarizability. The explanation for this is that the self-consistent-field algorithm used to determine the wave function gives a wave function which is self-consistent or precise to an extent ϵ , while the total energy determined in this method has an accuracy which goes as the square of the accuracy of the vectors i.e. as ϵ^2 . The dipole moment accuracy follows that of the vectors. These statements can be shown to follow rigorously as a consequence of the variational method used and as a consequence of Brillouins' theorem. At a latter stage in the present investigations we intend to examine this problem of the accuracy of the method and the applicability of Brillouins' theorem, especially for open shell atomic systems.

These results are to be compared with the results of other calculations for the polarizability of $F^{-}(^1S)$ as given in Table IV. The comparison shows that the polarizabilities calculated by the straightforward CHF procedure via a relatively ad hoc scheme of choosing the basis set agrees fairly well with the results of other methods at the same level of accuracy.

This procedure is now being applied to positive and negative ion states with s or p orbital open shells as well as closed shell systems. At the present time there is very little work on open shell systems²⁷ of ions.

V. Abstracts of Publications

The ${}^5\Pi_u - {}^5\Sigma_g^+$ Transition in N_2 , submitted to Mol. Phys.

Accurate electronic energy curves and wave functions of $1{}^5\Pi_u$ and $1{}^5\Sigma_g^+$ states of N_2 have been calculated using the multi-configuration self-consistent-field (MC-SCF) method. The ${}^5\Pi_u$ state was predicted by Mulliken, who suggested it was important in N_2 afterglow emissions. The calculated R_e and D_e of the ${}^5\Pi_u$ state is in reasonable accord with estimates of Carroll and Mulliken based on predissociative behavior of the $C{}^3\Pi_u$ state.

The vertical transition energy, ${}^5\Pi_u - {}^5\Sigma_g^+$, is calculated to be about 1.8-1.9 eV. The bound and resonance vibrational structure of the ${}^5\Sigma_g^+$ state are such that the transition would be observable as bound-like. The calculated transition probability is zero asymptotically but increases rapidly to shorter distances as the atoms overlap. At the vertical transition distance the transition probability is about $2 \cdot 10^5 s^{-1}$ or a lifetime of 5usec for the ground vibrational level.

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Table I. $F^{-}(^1S)$ basis set functions^(a)

Unperturbed atomic functions^(b)

n	l	Exponent
1	0	8.9165
1	0	14.7007
2	0	1.8485
2	0	3.2762
2	0	8.0477
2	1	0.9763
2	1	1.4496
2	1	2.0519
2	1	3.9288
2	1	8.2943

Polarization functions

Set I			Set II		
n	l	Exponent	n	l	Exponent
2	0	0.8243	3	0	1.6500
3	2	1.1540	3	2	0.7500
3	2	2.5990	3	2	1.0500
3	2	5.2190	3	2	1.5750
			3	2	2.4000
			3	2	3.7500
			4	3	0.9763
			4	3	2.0519

(a) For functions with quantum number l greater than zero both σ and π components were included.

(b) Hartree-Fock atomic basis taken from Ref. 26.

Table II. Results of polarizability calculation on $F^{-}(^1S)$ with basis set I. (a)

F	$\Delta E \times 10^6$ (b)	$\mu(F) \times 10^2$	$-Q \times 10^3$	$\Delta X \times 10^4$	$\mu(F)/F$	$-2\Delta E/F^2$	Q/F^2
0.0	0.0	0.0	0.0001245	0.0	---	---	---
0.0020	- 18.8057	1.87994	0.3421504	0.921	9.3997	9.4029	-85.538
0.0025	- 29.3843	2.35013	0.5350462	2.587	9.4005	9.4030	-85.607
0.0030	- 42.3147	2.82050	0.7711078	4.272	9.4017	9.4033	-86.678
0.0040	- 75.2324	3.76162	1.3723241	8.252	9.4040	9.4041	-85.765
0.0060	-169.3156	5.64586	3.093398	21.754	9.4098	9.4064	-85.928

(a) All quantities expressed in atomic units:

energy 1 a.u. = 27.21 eV, electric field 1 a.u. = 5.142×10^9 V/cm

dipole moment 1 a.u. = 2.541539 debyes, quadrupole moment 1 a.u. = 1.344911×10^{-26} esu-cm²

(b) $E(F=0.0) = -99.4593684872$ a.u.

Table III. Results of polarizability calculation on $F^{-}(^1S)$ with basis set II. (a)

F	$\Delta E \times 10^6$ (b)	$\mu(F) \times 10^2$	$-Q \times 10^3$	$\Delta X \times 10^4$	$\mu(F)/F$	$-2\Delta E/F^2$	Q/F^2
0.0	0.0	0.0	0.0001010	0.0	---	---	---
0.0020	-17.6301	1.76223	0.4535688	1.929	8.8112	8.8151	-113.392
0.0025	-27.5480	2.20344	0.7105004	3.196	8.8138	8.8154	-113.680
0.0030	-39.6707	2.64447	1.0237690	4.868	8.8149	8.8157	-113.752
0.0040	-70.5334	3.52714	1.8221216	9.948	8.8179	8.8167	-113.883

(a) All quantities in a.u. see Table II.

(b) $E(F=0.0) = -99.4593642991$ a.u.

Table IV. Polarizability calculations compared for F^{-1}

<u>Calculation</u>	<u>Ref.</u>	$\alpha(A^03)$
Yoshimine and Hurst UCHF	(28)	1.81
Donath CI + PT	(29)	1.206
Sternheimer SA	(30)	1.858
Langhoff and Hurst	(31)	1.902
Cohen CHF	(32)	1.560
Lahiri and Mukhirji SCPT	(33)	1.40
Present work (basis set I) CHF		1.39
Present work (basis set II) CHF		1.31

1 a.u. polarizability = .148176 A^03

UCHF: uncoupled Hartree-Fock calculation

CI-PT: perturbation theory via summation of series

SA: Sternheimer approximation

SCPT: Self consistent perturbation theory

List of Figures

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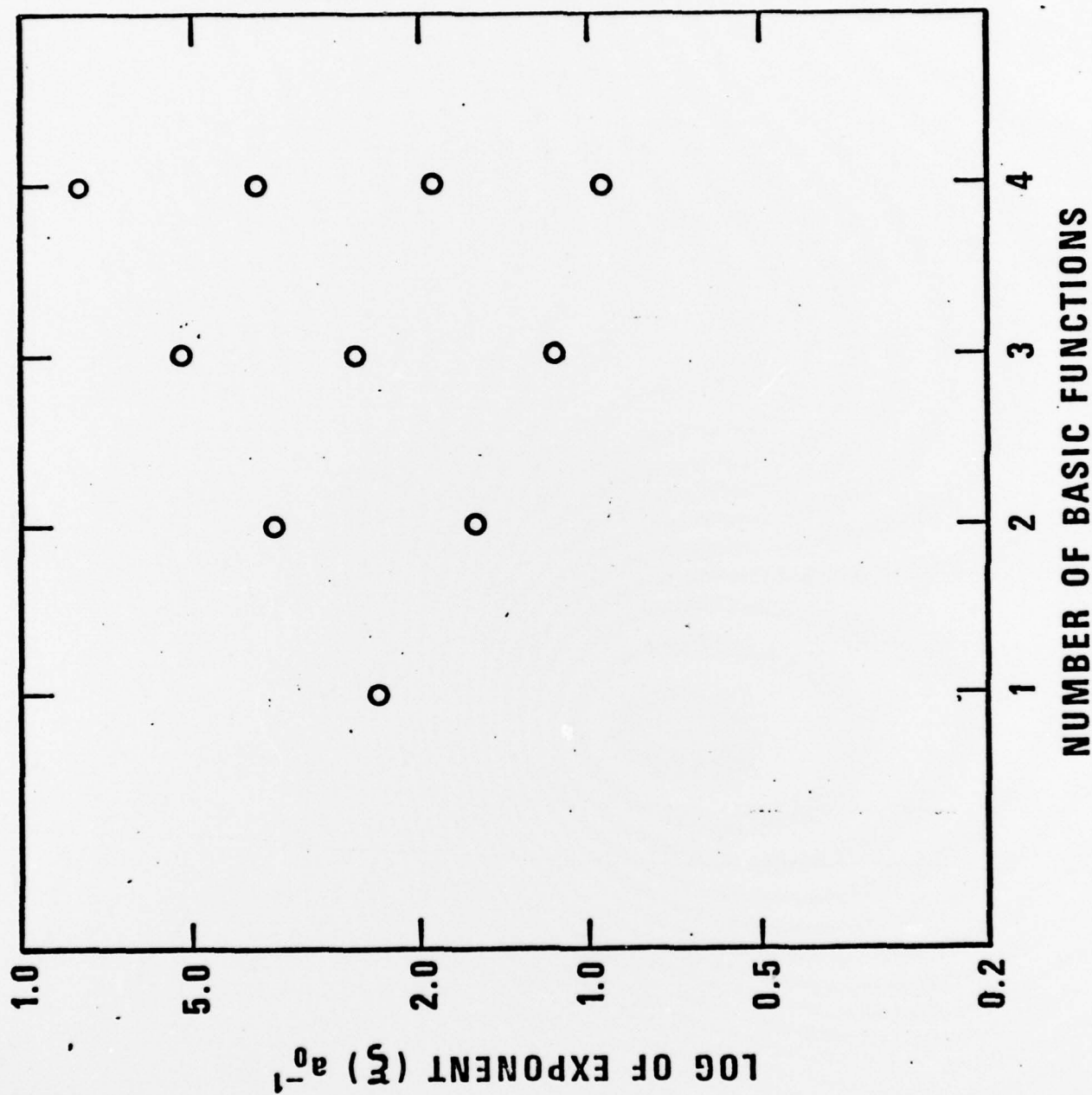
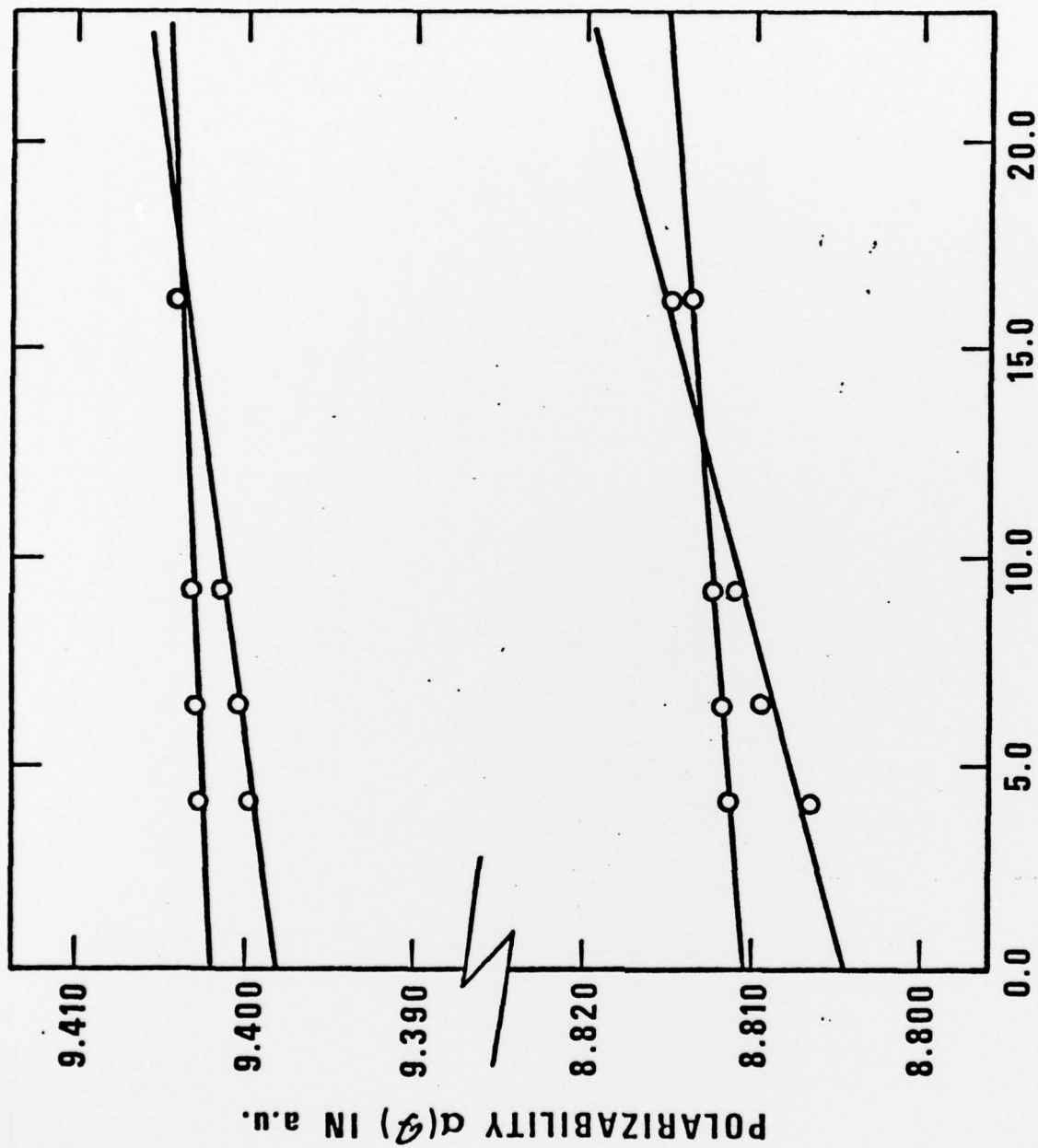


Figure 1. Plot of exponents, ξ , of STO's used to represent the 2p orbital of $F^-(1s)$ as a function of basis set size. Basis functions from Ref. 23.



$q^2 \times 10^6$ IN a.u.

Figure 2. Plot of $\alpha(F)$, the polarizability as a function of the square of the applied field. Plot A and B apply to basis set I, using expressions (7) and (11), respectively. Plot C and D apply to basis set II, using expressions (7) and (11), respectively. Units are atomic units; conversions are given in Table II.