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Coupled Multiconfigurational Self-Consistent-Field Method for Atomic Dipole Polarizabilities. II. Application to the First-Row Atoms, Lithium through Neon*

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Static dipole polarizabilities, accurate to within 5% are presented for the ground states and some valence excited states of the first-row atoms. The polarizabilities are obtained from multiconfigurational self-consistent-field wave functions, which were computed with the perturbing electric field included directly in the Hamiltonian. The use of the multiconfigurational framework allows any state of both degenerate and nondegenerate atoms to be considered, and also allows for the explicit introduction of electron-correlation effects. Detailed discussions of basis-set selection and the effects of electron correlation are presented along with comparisons with experimental and other theoretical polarizability results.

I. INTRODUCTION

In a previous paper[1] (hereafter referred to as Paper I), the coupled multiconfigurational self-consistent-field (CMCSCF) method for computing static atomic dipole polarizabilities was presented and applied to the ^1S, ^1D, and ^3P states of the neutral carbon atom. The CMCSCF method was shown to be a straightforward extension of the coupled Hartree-Fock (CHF) method,[2-4] in that both techniques involve the variational determination of a wave function for an atom in the presence of a perturbing electric field. However, the CMCSCF method possesses several powerful advantages by virtue of its multiconfigurational formalism: (i) Degenerate atoms are as easily treated as nondegenerate atoms: (ii) all states of the atom, including excited states, may be considered; and (iii) electron-correlation effects may be directly included if desired.

In the present work, the results of CMCSCF static-polarizability calculations are reported for the first-row atoms, lithium through neon. The polarizabilities have been computed at both the CHF level (i.e., only those configurations were employed to give the correct HF state of the atom), and at a level which includes the dominant atomic-correlation configurations for the particular atom.

The effect of electron correlation on the dipole polarizabilities of atoms may easily be studied with the CMCSCF technique, since it is an easy task to systematically add appropriate correlation configurations into the MCSCF calculation and note the degree of change in the resulting polarizability. In Paper I, the effect of correlation on the polarizability of carbon was studied to a limited degree utilizing additional configurations, which accounted for electronic rearrangements within the valence shell. To provide a more systematic prescription for treating the correlation problem as it applies to the atoms examined in this work, the carbon atom was further correlated with a large variety of potentially important terms.

In Sec. II of this paper, the formalism and computational details of the CMCSCF method are reviewed, with particular emphasis on the choice of a flexible basis set to adequately handle the polarization process. Section III is devoted to a discussion of the electron-correlation problem. Finally, the results of the CMCSCF polarizability calculations for the elements lithium through neon are reported in Sec. IV and compared to available experimental and other theoretical values.

II. REVIEW OF THE CMCSCF METHOD

A. General Formalism

In Paper I the equations and computational details of computing static atomic polarizabilities within the CMCSCF framework were treated in detail and only a brief review will be presented here. The basic approach to the calculation of dipole polarizabilities involves the determination of a wave function and an energy for an atom in the presence of a static electric field applied along the z axis of the atomic-centered coordinate system.[5] As shown below, the polarizability α of the atom can be determined either from the induced dipole moment (obtained from the wave function) or from the energy lowering relative to the unperturbed atom.

An MCSCF analysis of the perturbed atom system will yield a wave function which may be considered to be of the following form[6]:

$$\Psi_{\mathrm{CMC}} = \psi_0 + F\psi_1 , \tag{1}$$

where F is the magnitude of the perturbing field, ψ_0 is the unperturbed MCSCF wave function for an N-electron atom with Hamiltonian H_0 such that

$$(H_0 - E_0)\psi_0 = 0 , \tag{2}$$

and ψ_1 is the well-behaved solution of

$$(H_0 - E_0)\psi_1 + h\psi_0 = 0 , \tag{3}$$

with

$$h = -\sum_{i=1}^{N} \frac{\vec{\mathrm{F}} \cdot \vec{\mathrm{r}}_i}{F} . \tag{4}$$

In this framework, the static polarizability α becomes a function of the second-order change in the energy of the atom,[6]

$$\alpha = -2\langle \psi_0 | h | \psi_1 \rangle . \tag{5}$$

The electric field in the CMCSCF method is induced by a charge of magnitude Q' placed at varying distances along the z axis. This point-charge perturbation may be expanded in a series of inverse powers of R (charge-atom separation), as shown in Paper I, and after certain manipulations of Eqs. (1)–(5), a working expression is obtained for the polarizability:

$$\alpha(R) = (R^2/Q')\langle \Psi_{\mathrm{CMC}} | z | \Psi_{\mathrm{CMC}} \rangle + O(1/R^2) + \cdots . \tag{6}$$

The desired static polarizability then becomes the limiting value of $\alpha(R)$ as the field strength approaches zero (i.e., as R approaches infinity):

$$\alpha = \lim_{R \to \infty} \alpha(R) . \tag{7}$$

The quantity $\langle \Psi_{\mathrm{CMC}} | z | \Psi_{\mathrm{CMC}} \rangle$ is readily calculated from the final MCSCF wave function, and corresponds to the induced dipole moment of the atom due to the field.

In addition to this induced dipole moment, the MCSCF analysis also yields a total energy E_{CMC} which is defined by

$$E_{\mathrm{CMC}}(R) = \langle \Psi_{\mathrm{CMC}} | H_0 + Fh(R) | \Psi_{\mathrm{CMC}} \rangle , \tag{8}$$

from which one may obtain the energy of interaction, ΔE, between the atom and the field, i.e.,

$$\Delta E = E_{\mathrm{CMC}} - E_0 , \tag{9}$$

where E_0 has been defined by Eq. (2). It was shown in Paper I that the polarizability could also be expressed as a function of ΔE [see Eq. (17), Paper I], but that obtaining α from the induced dipole moment is numerically a more satisfactory procedure, which is in agreement with a similar conclusion reached by Cohen and Roothaan[2] in their discussion of the CHF method.

B. Computational Methods

The calculations reported in this work were performed with the BISON[7] Slater-type orbital (STO) integral and HF-SCF program and the BISON-MC[8] MCSCF system developed by Wahl and Das. The BISON-MC program variationally determines a wave function which is expressed as a linear combination of Slater determinants in terms of molecular-spin orbitals (MSO's). The MSO's are ultimately expressed as a linear combination of atomic-centered STO's. The choice of this STO basis set will be discussed in Sec. II C.

In actual practice, the BISON-MC program is used to generate a wave function for the atom in the presence of a perturbing field. The polarizability is then given as a function of the induced dipole moment, as shown in Eq. (6). To obtain the limiting value of $\alpha(R)$ as the field strength approaches zero, the charged particle is systematically removed from the atom until the results at two successive points agree to within a given tolerance. Generally speaking, for the majority of the first-row atoms treated in this work, the magnitude of the charge was taken to be unity (i.e., a proton) and the calculated polarizability normally reached a limiting value around $R=$ 18 a.u. However, for those atoms, such as lithium, that possess large polarizabilities, the convergence was considerably slower as a function of R.

The electronic configurations employed in the MCSCF wave function include the base configurations, which are those required to give the correct asymptotic HF state of the particular atom, plus additional correlation terms. The various types of correlation configurations and their effect on the dipole polarizabilities will be discussed in Sec. III.

It should be pointed out that all calculations were performed in $C_{\infty v}$ symmetry. The asymptotic behavior of $C_{\infty v}$ wave functions approaching the corresponding state of the spherical atom, and the resulting manifestations observed in properties such as the total energy and dipole polarizability, were examined in detail in Paper I. The subject will not be discussed further in the present work except as it relates to the correlation problem, which is covered in Sec. III.

C. Choice of Basis Functions

As pointed out in Sec. II B, the solution of MCSCF equations in the OVC program entails the variational determination of a set of optimized

MO's, which are given as a linear combination of STO's. In computing polarizabilities via such an expansion method, the normal procedure[3,4] involves use of an accurate HF atomic basis set, augmented by an appropriate set of polarization functions. The choice of the polarization functions is particularly critical, since the resulting polarizability is directly dependent on the flexibility allowed in the wave function to properly describe the distortion of the atom in the presence of the perturbing electric field.

Sitter and Hurst[4] have reported rules for specifying the principal quantum number and spherical harmonic portions of the polarization functions, which leaves only the exponents of the radial terms to be determined. In Paper I a simple procedure was described which is based on the minimization of a one-electron perturbation function coupling the polarization function and the unperturbed atomic function. It was also shown that this technique yields radial exponents that are within 5% of exponents obtained from more costly brute-force optimization techniques. Any residual error due to the approximate nature of the exponents should be minimized by the fact that several polarization functions of each type are added to the atomic basis sets.

Thus for the calculations reported in this work, the basis sets consist of an accurate HF set, augmented with several additional functions required to properly account for electron-correlation effects, and finally a set of polarization functions chosen in accord with Sitter and Hurst's rules, and with radial exponents determined by application of Eq. (18) in Paper I.

A question now arises concerning the flexibility of these basis sets in producing reliable polarizabilities. In Paper I it was shown that the polarization functions for helium and beryllium agreed well with those obtained by Cohen via an arduous exponent-optimization procedure. In addition, our final calculated polarizability for neon agrees perfectly with the polarizability obtained by Kaneko and Arai,[9] using a numerical CHF technique. Finally, for beryllium, the polarization basis was further augmented with three more $3d$ functions, two more $3s$ functions, and two additional $2p$ functions. The resulting polarizability from the large basis was 5.43 Å^3, as compared to 5.41 Å^3 with the smaller set. A similar study was performed on the carbon atom and was described in Paper I. Hence, it is not unreasonable to assume that our basis sets contribute no more than 2 or 3% error to the calculated polarizabilities.

TABLE I. Effect of electron correlation on carbon ^3P polarizability.

Configurations in MCSCF[a]	Calculated α (Å^3)
$1s^22s^22p^2$ (base configuration)	1.49
Base $+1s^22p^4$ (valence-shell doubles)	1.42
Base $+1s^22p^4+1s^22s2p^23d$ (semi-internal)	1.41
Base $+1s^22p^4+1s^22s2p^23d+$ $1s2s^22p^3+1s^22s^22p3d$ (odd parity)	1.45

[a] Configurations listed above were included in MCSCF calculation in all possible symmetry-allowed coupling schemes.

III. ELECTRON-CORRELATION EFFECTS

A. General

For the first-row atoms, it is well established that a significant portion of the electron-correlation effects may be handled by considering the correlation from excitations within the valence shell and the most important portions of the "semi-internal" correlations,[10-12] which correspond to single excitations with a spin flip to orbitals outside the valence shell. In Paper I the effect of the valence-shell correlation on the dipole polarizability of the carbon atom was reported, indicating that such terms lowered the calculated polarizability by between 5 and 10% relative to the base-configuration results. In order to provide a sounder basis for including correlation in the other first-row atoms reported in this work, a more detailed study of correlation terms seemed appropriate.

Before the results of this study are presented, it is instructive to consider qualitatively the possible refinements to dipole polarizabilities computed at the CHF level by the addition of the correlation terms. From consideration of Brillouin's theorem[13] and the work of Moller and Plesset,[14] it is obvious that when the SCF equations for the atom are solved using the full Hamiltonian for the sytem (i.e., in the present case, when the external field is included in the Hamiltonian), any corrections to one-electron properties due to correlation, such as the dipole polarizability, will appear as higher-order terms, if such were considered in a perturbative formalism. Thus, it is not surprising that atomic polarizabilities calculated in the CHF formalism have normally agreed well with available experimental data. This situation is to be contrasted to schemes where both the correlation and the external field are treated as perturbations on a zeroth-order atomic wave function. All calculations of that type require corrections to the wave function in first order. Hence, it is anticipated that the effect of electron correlation on polarizabilities computed in the CMCSCF formalism would be small relative to the base-configuration results, mainly owing to the inclusion of the external field in the Hamiltonian.

Another point that deserves mention concerns the treatment of the charge-atom system in $C_{\infty v}$ symmetry. When the spherical atomic symmetry is relaxed to $C_{\infty v}$, even-parity (with respect to the original atomic symmetry) basis functions are allowed to mix with the spherical atomic SCF solutions. In a restricted sense, this corresponds to the inclusion of other configurations in the calculation, many of which correspond to important correlation terms. Thus, the CMCSCF base-configuration results do, in certain cases, have some "correlation" effects included simply owing to the symmetry relaxation. This situation was examined in detail in Paper I.

B. Effect of Correlation on Carbon

To provide the basis for including correlation in the CMCSCF calculations on the first-row atoms, the polarizability of carbon was studied as a function of the various types of possible correlation contributions. Basically, with the help of accurate atomic CI wave-functions,[10,11] the choice of important configurations in carbon was narrowed down to three types: (i) valence-shell double-excitation terms, e.g., $1s^22s^22p^2$-$1s^22p^4$; (ii) semi-internal terms, e.g., $1s^22s^22p^2$-$1s^22s2p^23d$; and (iii) various energetically favorable odd-parity terms rendered symmetry allowed by the presence of the charge, e.g., $1s^22s^22p^2$-$1s^22s2p^3$. To ascertain the effect of these terms on the polarizability, the various types of configurations mentioned above, in all possible coupling schemes, were systematically added to the $^3P(M_L=0)$ base configuration of carbon. The results of this study are presented in Table I. It is immediately obvious that conclusions reached in Sec. III A are borne out by the results in this table. The correlation terms affect the polarizability computed at the base-configuration level by only about 5–10%. It is also apparent that the valence-shell double configurations have the greatest effect and lower the polarizability by about 10%. The semi-internal contribution is small, as is the contribution from the odd-parity terms. Based on this analysis, it was decided that the addition of valence-double and semi-internal configurations would be sufficient to obtain a reasonably accurate description of the correlation effects for the other first-row atoms. However, in cases of near degeneracies in the valence shell, such as in beryllium, the odd-parity configurations were again added to ensure completeness.

The configurations and final perturbed-atom

TABLE II. Perturbed-atom CMCSCF configurations and mixing coefficients.[a]

Atom (state)	Configurations	Open-shell couplings[b]	Mixing coefficients
Lithium ($^2\Sigma^+$)	$1s^22s$	$^2\Sigma$	1.000 00
Beryllium ($^1\Sigma^+$)	$1s^22s^2$		0.950 36
	$1s^22p_\sigma^2$		−0.180 69
	$1s^22p_\pi^2$	$^1\Sigma$	−0.253 31
	$1s^22s2p_\sigma$	$^2\Sigma\rightarrow{}^1\Sigma$	−0.000 01
Boron ($^2\Sigma^+$)	$1s^22s^22p_\sigma$	$^2\Sigma$	0.963 96
	$1s^22p_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^2\Sigma$	−0.226 34
	$1s^22s2p_\sigma3d_\sigma$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\Sigma$	0.075 49
	$1s^22s2p_\sigma3d_\sigma$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\Sigma$	−0.047 01
	$1s^22s2p_\pi3d_\pi$	$^2\Sigma\rightarrow{}^1\pi\rightarrow{}^2\Sigma$	−0.082 88
	$1s^22s2p_\pi3d_\pi$	$^2\Sigma\rightarrow{}^3\pi\rightarrow{}^2\Sigma$	0.069 09
Boron ($^2\pi$)	$1s^22s^22p_\pi$	$^2\pi$	0.968 11
	$1s^22p_\sigma^22p_\pi$	$^2\pi$	−0.166 42
	$1s^22p_\pi^3$	$^2\pi$	0.158 09
	$1s^22s3d_\sigma2p_\pi$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\pi$	0.057 92
	$1s^22s2p_\sigma3d_\pi$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\pi$	−0.061 90
	$1s^22s2p_\sigma3d_\pi$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\pi$	0.053 78
Nitrogen ($^4\Sigma^-$)	$1s^22s^22p_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^4\Sigma$	0.992 76
	$1s^22s2p_\sigma3d_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\Sigma\rightarrow{}^4\Sigma$	−0.035 40
	$1s^22s2p_\sigma3d_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^4\Sigma\rightarrow{}^4\Sigma$	0.058 32
	$1s^22s2p_\sigma3d_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\Sigma\rightarrow{}^4\Sigma$	0.014 31
	$1s^22s2p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^3\pi\rightarrow{}^4\Sigma$	0.069 39
	$1s^22s2p_\sigma^22p_\pi3d_\pi$	$^2\Sigma\rightarrow{}^3\pi\rightarrow{}^4\Sigma$	0.068 89
Oxygen ($^3\Sigma^-$)	$1s^22s^22p_\sigma^22p_\pi^2$	$^3\Sigma$	0.995 73
	$1s^22s2p_\sigma^23d_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^3\Sigma$	0.014 62
	$1s^22s2p_\sigma^23d_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^3\Sigma$	−0.060 39
	$1s^22s2p_\sigma2p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\pi\rightarrow{}^3\Sigma$	0.055 56
	$1s^22s2p_\sigma2p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^4\pi\rightarrow{}^3\Sigma$	−0.037 15
	$1s^22s2p_\sigma3p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\pi\rightarrow{}^3\Sigma$	−0.014 02
Oxygen ($^3\pi$)	$1s^22s^22p_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^3\pi$	0.996 34
	$1s^22s2p_\sigma3d_\sigma2p_\pi^2$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\Sigma\rightarrow{}^3\pi$	−0.043 03
	$1s^22s2p_\sigma3d_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^4\Sigma\rightarrow{}^3\pi$	0.023 45
	$1s^22s2p_\sigma3d_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\Sigma\rightarrow{}^3\pi$	0.029 24
	$1s^22s2p_\sigma^22p_\pi^23d_\pi$	$^2\Sigma\rightarrow{}^2\Sigma\rightarrow{}^3\pi$	−0.028 32
	$1s^22s2p_\sigma^22p_\pi^23d_\pi$	$^2\Sigma\rightarrow{}^4\Sigma\rightarrow{}^3\pi$	−0.025 27
	$1s^22s2p_\sigma^22p_\pi^23d_\pi$	$^2\Sigma\rightarrow{}^2\Sigma\rightarrow{}^3\pi$	0.029 19
	$1s^22s2p_\pi^43d_\pi$	$^2\Sigma\rightarrow{}^3\pi$	−0.041 87
Fluorine ($^2\Sigma^+$)	$1s^22s^22p_\sigma2p_\pi^4$	$^2\Sigma$	0.995 26
	$1s^22s2p_\sigma3d_\sigma2p_\pi^4$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\Sigma$	0.014 39
	$1s^22s2p_\sigma3d_\sigma2p_\pi^4$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\Sigma$	−0.077 81
	$1s^22s2p_\sigma^22p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^1\pi\rightarrow{}^2\Sigma$	0.047 79
	$1s^22s2p_\sigma^22p_\pi^33d_\pi$	$^2\Sigma\rightarrow{}^3\pi\rightarrow{}^2\Sigma$	−0.030 34
Fluorine ($^2\pi$)	$1s^22s^22p_\sigma^22p_\pi^3$	$^2\pi$	0.999 48
	$1s^22s2p_\sigma^23d_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^1\Sigma\rightarrow{}^2\pi$	−0.001 76
	$1s^22s2p_\sigma^23d_\sigma2p_\pi^3$	$^2\Sigma\rightarrow{}^3\Sigma\rightarrow{}^2\pi$	0.032 11
Neon ($^1\Sigma^+$)	$1s^22s^22p_\sigma^22p_\pi^4$		1.000 00

[a] Slater orbital expansions for the orbitals determined in the CMCSCF calculations reported here have been deposited with the National Auxiliary Publications Service (NAPS). For a copy of these tabulations order NAPS document No. 02201 for 16 pages of supplementary material. Order from ASIS/NAPS c/o Microfiche Publications, 305 E. 46th St., New York, N.Y. 10017. Remit in advance for each NAPS accession number $1.50 for microfiche or $5.00 for photocopies up to 30 pages, 15¢ for each additional page. Make checks payable to Microfiche Publications.

[b] These symbols represent the left-to-right vector sums of the spins and orbital angular momenta of the open shells in the configuration (i.e., the coupling of each open shell with the total spin and angular momentum of the open shells preceding it).

configuration mixing coefficients for all of the first-row atoms in this study are given in Table II.

IV. CMCSCF POLARIZABILITY RESULTS

A. *S*-State Atoms: Li, Be, and Ne

Lithium and neon are the simplest first-row atoms to treat with the CMCSCF method. Both atoms possess ground *S*-states, and hence only one cylindrical state need be considered in the calculation of the polarizability. In addition, the important valence-double excitation is not possible for either atom, so correlation effects are expected to be unimportant. Thus, our calculations were performed at the CHF level with only single-configuration wave functions. There have been many other theoretical calculations on Li and Ne, and our results are compared to these and the most reliable experimental values in Table III. The excellent agreement is not surprising, in light of the above considerations.

In the case of neon, it is particularly important to note that the CMCSCF calculation agrees perfectly with the numerical CHF treatment of Kaneko and Arai,[9] and also the CHF calculation of Sitter and Hurst,[4] which used a much larger polarization basis than the one employed here. As mentioned previously, this result certainly supports the reliability of the polarization-function-exponent-determination method that was described in Paper I. Although our value for α(Ne) in Table III is in excellent agreement with other theoretical values, it is somewhat below the experimental number obtained by Dalgarno[15] from index-of-refraction data. We are in good agreement, however, with the value of 0.342 ± 0.011 Å^3 deduced by Hackam[16] from ion-mobility measurements.

Matsubara *et al.*[17] have used MBPT to compute a value for the polarizability of neon which is in excellent agreement with the result deduced from index-of-refraction data (see Table III). Their calculation, however, was only done to first order, and did not include the higher-order diagrams necessary to describe the full interaction of the atom with the perturbing field or the two-electron-correlation effects. If we restrict the CMCSCF method to include only single excitations from the frozen Hartree-Fock configuration (as opposed to the fully coupled calculations we have reported in Table III), the computed polarizability is 0.381 Å^3, which is considerably larger than the fully coupled value of 0.351 Å^3. Although this is not an exact simulation of the first-order MBPT calculation, it is a good indication that the restriction to single excitations can lead to a poor approximation to the fully coupled result.

In a further attempt to resolve the discrepancy between our single-configuration results and the experimental value for neon, we added some correlating configurations to the neon wave func-

TABLE III. CMCSCF polarizability results for Li, Be, and Ne.

Atom	State	CMCSCF results Base	Correlated	Other values [a] α (Å^3)	Method	Ref.
Li	^2S	25.37	25.37[b]	25.23	Variation perturbation	20
				24.96	Double perturbation	21
				24.84	MBPT	22
				22 ± 2	Atomic-beam deflection	23
Be	^1S	6.75	5.41[c]	6.24	PUCHF	24
				6.76	CHF	3
				6.93	MBPT	18
				5.42	Hylleras variation perturb.	19
				5.54	PUCHF	25
				5.49	Perturb. var. with CI	26
Ne	^1S	0.351	0.351[b]	0.352	CHF	4
				0.349	PUCHF	27
				0.349	Numerical CHF	9
				0.395	MBPT	17
				0.395	Index of refraction	15
				0.342	Ion mobilities	16

[a] Other values not listed in table may be found in review by Teachout and Pack, Ref. 28.

[b] Results at the CHF level; i.e., single-configuration wave function only.

[c] Calculated with base configuration plus valence-shell doubles and odd-parity terms as listed in text.

tion. First, the neon basis was augmented with STO's appropriate for correlation. Configurations consisting of double excitations from the p orbitals were then added to the single-configuration wave function. Weiss[10] has shown that double excitations of this type account for a large portion of the valence-correlation energy in neon. The CMCSCF polarizability obtained from the correlated wave function (0.354 $Å^3$) differed negligibly from the single-configuration result reported in Table III. A more detailed investigation of the effect of electron correlation on the polarizability of neon, which is beyond the scope of the present work, is needed to verify the accuracy of our computed value in this case.

Beryllium is one of the more unusual atoms in the first row, owing to the near degeneracy of its ground state ($1s^2 2s^2$, ^1S) with three other singlets: ($1s^2 2p^2$, ^1S), ($1s^2 2p^2$, ^1D), and ($1s^2 2s 2p$, ^1P). It is therefore important that all of these terms be included in the wave function in order to obtain a reliable description of the charge distribution, and ultimately, the dipole polarizability. The ^1S ground state projects into only one cylindrical state ($^1\Sigma^+$). Hence, to form the MCSCF wave function, the $^1\Sigma^+$ projections of the four states listed above were employed. The results of the CMCSCF calculations are presented in Table III. The single-determinant base-configuration result of 6.75 $Å^3$ agrees well, as it should, with Cohen's CHF results.[3] The correlated value of 5.41 $Å^3$ exhibits a marked lowering relative to the base-configuration value, and is due almost entirely to the large mixing of the ($1s^2 2p^2$, ^1S) and ($1s^2 2p^2$, ^1D) configurations. The ($1s^2 2s 2p$, ^1P) configuration was also present in this calculation, but the mixing was small compared to the valence-double terms.

The correlated beryllium polarizability exhibited the largest lowering of any of the first-row-atom polarizabilities as a result of inclusion of the valence-double terms. At first, the result was somewhat bothersome, particularly in light of Kelly's MBPT[18] value of 6.93 $Å^3$, which also accounts for correlation. Hence, as a check, the calculation was repeated with a largely expanded polarization basis, but this resulted in a negligible change in the polarizability (5.43 $Å^3$). Recently, Sims and Rumble[19] have calculated the dipole polarizability of beryllium, using the

TABLE IV. CMCSCF polarizability results for B, C, N, O, F.

		α(CMCSCF)($Å^3$)			Other values [a]		
Atom	State	α(base)	α(corr.) [b]	α(avg.) [c]	α($Å^3$)	Method	Ref.
B	$^2P(^2\Sigma^+)$	4.03	3.44	2.85	2.93	Coupled variation perturbation	20
	$^2P(^2\pi)$	2.89	2.56		4.18	Sternheimer perturbation	30
C	$^1S(^1\Sigma^+)$	1.82	1.77	1.77			
	$^1D(^1\Sigma^+)$	1.98	1.93	1.69			
	$^1D(^1\pi)$	1.79	1.76				
	$^1D(^1\Delta)$	1.57	1.51				
	$^3P(^3\Sigma^-)$	1.49	1.42	1.66	1.54	(^3P) MBPT	31
	$^3P(^3\pi)$	1.88	1.78		1.75	(^3P) Approximate UCHF	32
N	$^4S(^4\Sigma^-)$	1.02	1.02	1.01	1.04	(^4S) Approximate UCHF	32
	$^2D(^2\Sigma^-)$	1.08	1.08	1.07	1.13	(^4S) Optical interferometry	33
	$^2D(^2\pi)$	1.06	1.05		1.30	(^4S) Antisymmetrized Hartree	6
	$^2D(^2\Delta)$	1.07	1.07				
	$^2P(^2\Sigma^+)$	1.11	1.07	1.05			
	$^2P(^2\pi)$	1.12	1.04				
O	$^1S(^1\Sigma^+)$	0.75	0.71	0.71	0.83	(^1S) MBPT to 2nd order	34
	$^1D(^1\Sigma^+)$	0.67	0.66	0.70			
	$^1D(^1\pi)$	0.68	0.68		0.79	(^1D) MBPT to 2nd order	34
	$^1D(^1\Delta)$	0.75	0.75				
	$^3P(^3\Sigma^-)$	0.75	0.74	0.69	0.78	(^3P) MBPT to 2nd order	34
	$^3P(^3\pi)$	0.67	0.66		0.77 ± 0.06	Optical interferometry	33
F	$^2P(^2\Sigma^+)$	0.46	0.44	0.47	0.53	Approximate UCHF	32
	$^2P(^2\pi)$	0.50	0.48		0.60	Antisymmetrized Hartree	6

[a] Other values not listed in table may be found in review by Teachout and Pack, Ref. 28.

[b] Calculated with base configuration plus valence-shell doubles and semi-internals where possible.

[c] Value for atomic state computed as a spherical average over the various cylindrical M_L projections.

Hylleras variation-perturbation scheme[29] on a highly accurate Hylleras-type beryllium wave function. They compute a polarizability of 5.42 ±0.05 Å^3, with a rigorous lower bound of 5.30 Å^3, which is in excellent agreement with the CMCSCF result. Since the Sims and Rumble calculation is probably the most accurate treatment of beryllium to date, the CMCSCF beryllium polarizability appears to be reliable. There are no experimental values available for comparison.

B. Results for Open-Shell Atoms: B, C, N, O, F.

For the open-shell atoms of the first row in other than S states, the full diagonal polarizability tensor for the particular state must be computed. That is, the dipole polarizabilities must be computed for each of the M_L projections arising from a given state, which may then be spherically averaged to yield the average static polarizability $\overline{\alpha}$. This requirement is easily handled in the CMCSCF formalism, since the M_L substates arise naturally from use of the $C_{\infty v}$ coordinate system.

To account for electron correlation, all possible valence-double and semi-internal-type configurations were considered in the CMCSCF determination of the wave functions. In addition to the ground states of the atoms, any excited states arising from the ground electron configuration have also been treated. The CMCSCF results for the open-shell atoms are displayed in Table IV and compared to other theoretical values and available experimental data.

Of the results presented in Table IV, those for the ^2P ground state of boron exhibit the largest anisotropic effect. The base-configuration results are 4.03 Å^3 for the $M_L = 0$ state and 2.89 Å^3 for the $M_L = \pm 1$ state, which yield an $\overline{\alpha}$ (base) of 3.27 Å^3, which is in fair agreement with the result of Mukherjee *et al.*[20] via a HF-level coupled variation-perturbation treatment. The only other boron polarizability available for comparison at the base-configuration level is that of Tiwari *et al.*,[30] which is probably too large (4.18 Å^3), possibly owing to an insufficiently accurate zeroth-order function in their Sternheimer perturbation[35] analysis. When valence-double ($1s^2 2p^3$) and semi-internal ($1s^2 2s 2p 3d$) correlation contributions are included in the analysis, the resulting polarizabilities are 3.44 Å^3 and 2.56 Å^3 for the $M_L = 0$ and $M_L = \pm 1$ components, respectively, which yield an $\overline{\alpha}$ of 2.85 Å^3. This represents a decrease of approximately 14% relative to the base-configuration value, and is consistent with the effect of the valence-double term on the dipole polarizabilities of other first-row atoms. Unfortunately, neither theoretical values at the correlated level nor experimental figures are available with which to compare the CMCSCF correlated polarizability for boron.

As pointed out above, the anisotropy in the calculated polarizability-tensor components of boron is the largest observed in the first-row atoms. It is interesting to note that the polarizability anisotropy of the ($6s6p\,^3P_2$) state of metastable mercury has been determined experimentally using the atomic beam E-H gradient-balance method,[36] which indicates that the anisotropic effects exhibited in the CMCSCF calculations would possibly be experimentally confirmed at some future date.

The CMCSCF results for the ^1S, ^1D, and ^3P states of carbon were discussed in detail in Paper I, and are included in Table IV of this work for completeness only. As pointed out in Paper I, the CMCSCF correlated $\overline{\alpha}$ and its tensor components for the ^3P state of carbon are in excellent agreement with Miller and Kelly's figures[31] obtained from a MBPT analysis carried through fourth order. No experimental values are available for comparison.

The ground-state configuration of nitrogen ($1s^2 2s^2 2p^3$) yields three possible states, the ^4S ground state and the ^2P and ^2D excited states. The correlated $\overline{\alpha}$ for the ^4S state is 1.01 Å^3, which is in excellent agreement with value obtained by Thorallsson *et al.*[32] of 1.04 Å^3 via an approximate UCHF treatment. The only other theoretical value available is 1.3 Å^3 obtained by Dalgarno[6] from an antisymmetrized Hartree approximation. Both the CMCSCF and approximate UCHF results are in very good agreement with the experimental result for the ^4S state of 1.13 ±0.06 Å^3, determined by optical interferometry.[33] It should be noted that there is no possible valence-double configuration with the correct symmetry to mix with the ^4S ground state of nitrogen. This is probably the main reason why the other theoretical results, which do not contain any correlation effects, are in such close agreement with the CMCSCF figure and the experimental number for this state. The only substates of nitrogen where the valence-double term is symmetry allowed occur in the ^2D and ^2P excited states. No experimental determinations have been made on these states for comparison.

For oxygen, Kelly[34] has reported MBPT results for the ^1S, ^1D, and ^3P states. His values are compared to the CMCSCF results and to the experimental value of 0.77 ± 0.06 Å^3, from optical-interferometry measurements,[33] in Table IV. The CMCSCF polarizabilities are approximately 10% lower than those obtained from MBPT, but it should be noted that the reported MBPT numbers were only calculated to second order. Acutally, Kelly carried the analysis to third order, but then reasoned that the fourth-order terms would approximately cancel the third-order lowering and hence the second-order figures were taken as final. Miller and Kelly's recent and more accurate analysis on carbon[31] appears to contradict such reasoning, in that their calculated fourth-order contribution to $\overline{\alpha}$ is only about 25% of the third-order term. If the calculated third-order contribution to $\overline{\alpha}$ for the ^3P state of oxygen is subtracted from the second-order value, the result is 0.64 Å^3. The projected raising of this number due to fourth-order diagrams based on analogy with the carbon treatment would bring Kelly's $\overline{\alpha}$ for ^3P oxygen into excellent agreement with the CMSCF value of 0.69 Å^3. Both the MBPT and CMCSCF polarizabilities for the ^3P state of oxygen are in excellent accord with the experiment.

The ground state of fluorine ($1s^22s^22p^5\,^2P$) possesses no possiblity for the normally important valence-double term, and hence only the semi-internal correlation configurations ($1s^22s2p^53d$) were employed in the MCSCF analysis. The CMCSCF calculated $\overline{\alpha}$ is 0.47 Å^3, which agrees well with the value of 0.53 Å^3 from an approximate UCHF treatment.[32] Unfortunately, no experimental information is available for comparison.

V. CONCLUSIONS

The results presented in Sec. IV indicate that the CMCSCF method is a powerful and promising tool in the determination of reliable atomic-dipole polarizabilities. The agreement with experiment and other accurate theoretical treatments which account for correlation is quite good. At this point it is appropriate to make estimates of possible errors in the CMCSCF results. To begin with, there is, of course, the question of completeness of the basis set, particularly with regard to the polarization functions. The agreement of the CMCSCF and numerical CHF results for neon, and the basis-set-convergence studies on beryllium and carbon, appear to indicate that errors in the final polarizabilities due to the basis set should be no larger than 2 or 3% in the most severe cases. This possible error is always in the direction such that any improvement in the basis set would tend to increase the calculated polarizability.

The other source of error is due to any significant components of electron correlation that have been neglected in the determination of the wave function. The correlation contributions included in the results reported in this work were chosen by an analysis of large CI atomic wave functions[10,11] and the study of the effect of correlation on the carbon polarizability discussed in Sec. III B. Considering the analysis presented in Sec. III A and the fact that the most important correlation contributions have been included in the wave functions, it is not unreasonable to postulate a maximum error of 3–5% from neglect of higher-order correlation terms. It is somewhat difficult to ascertain the direction this error might take, but limited experience thus far indicates that further correlation usually lowers the calculated polarizabilities, which would tend to cancel some of the errors due to the basis sets. Thus the CMCSCF results reported in this work are ascribed uncertainties on the order of ±5%.

Finally, a few comments are appropriate concerning the flexibility and general applicability of the CMCSCF method for determining atomic polarizabilities, particularly as compared to other techniques currently being used for this purpose. In general terms, the most popular techniques for determining dipole polarizabilities include the CHF method,[2-4] the uncoupled Hartree-Fock (UCHF) method,[37-40] various perturbative UCHF schemes[24,25,41] (PUCHF), and many-body perturbation theory (MBPT).[18,22,31,34]

The CHF method has produced reasonably accurate results, which is not surprising in light of Brillouin's theorem[13,14] and the fact that the wave function is obtained self-consistently with a Hamiltonian that includes the external field. However, CHF methods generally have not been applied to open-shell atoms possessing more than one cylindrical angular momentum state. Also, by definition, the CHF methods do not provide for the inclusion of electron-correlation effects. The CMCSCF method has overcome both of these problems within the framework of existing diatomic MSCSF technology.

To avoid the supposed computational effort and limitations of the CHF scheme, various UCHF and PUCHF methods were developed which basically start with atomic HF wave functions and add the corrections perturbatively. Even though such techniques require less labor than CHF treatments and have produced good results for selected systems, they must still be considered as approximations to the CHF technique. In addition, proper treatment of open-shell atoms and electron correlation has turned out to be nearly as difficult in the UCHF formalism as in the CHF method.

Many-body perturbation theory and perturbation theory using correlated zeroth-order wave functions compare most favorably with the CMCSCF method in terms of ultimate accuracy. These techniques, however, appear to be more complex and more prone to difficulties in pathological systems such as beryllium.

In addition to being very flexible, the CMCSCF method is rather inexpensive, once the MCSCF technology is provided. Since the only basis functions are centered on the atom, the two-electron integrals required for the calculations are all of the one-center variety and may be computed once and then reused for other charge-atom distances. The only integrals that need to be recomputed as a function of R are the nuclear-attraction terms, which involve basis functions on the atom and the external charge. Also, since there are no drastic charge rearrangements in the atom under the influence of the perturbing field, the MCSCF analysis converges rapidly, even in cases where a large number of correlation configurations are included in the wave function.

The CMCSCF method is applicable to molecules as well as atoms. Work is currently underway to determine the longitudinal and transverse polarizabilities of first-row diatomics. Also, since large basis sets of Slater-type orbitals can become prohibitively expensive, and investigation of the use of Gaussian orbitals in the determination of molecular polarizabilities is being undertaken.

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