PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOL. 6, NO. 3 SEPTEMBER 1972

Coupled Multiconfigurational Self-Consistent-Field Method for Atomic Dipole Polarizabilities. I. Theory and Application to Carbon

Frank P. Billingsley, II* and Morris Krauss†
National Bureau of Standards, Washington, D. C. 20234
(Received 10 April 1972)

A method for calculating static dipole polarizabilities of atoms within a multiconfigurational self-consistent-field (SCF) framework is presented. The method involves the direct solution of the multiconfigurational SCF equations of an atom in the presence of a perturbing field which is simulated by a charged particle. The use of a multiconfigurational framework allows this technique to be applied straightforwardly to any given state of both degenerate and nondegenerate atoms, and also allows the explicit introduction of correlation effects. Sample calculations are reported for the static dipole polarizabilities of the carbon atom in its ^1S, ^1D, and ^3P states with partial inclusion of correlation. The results are compared with those obtained from many-body perturbation theory, and other techniques. In addition, a prescription for specifying a sufficiently flexible set of polarization basis functions is described.

I. INTRODUCTION

Static dipole polarizabilities of atoms[1] have been calculated from the coupled Hartree-Fock (CHF) method,[2-5] the coupled Hartree-Fock perturbation (CHFP) method,[6-8] the double perturbation theory,[9-11] and the many-body perturbation theory (MBPT).[12-14] Essentially, the perturbation techniques normally use Hartree or Hartree-Fock atom solutions as zeroth-order functions from which the first-order perturbed function for the atom in a field may be obtained. The polarizability is then expressed as a function of the change in the second-order energy of the isolated atom.[15] On the other hand, the CHF method consists of variationally solving the HF equations for an atom in the presence of a finite field. The polarizability may then be expressed either as a function of the induced dipole moment or as a function of the second-order change in the energy. In the limit of a vanishing field, the CHF method becomes equivalent to the CHFP method.

In the present work, we report a scheme for the calculation of atomic polarizabilities within a multiconfigurational self-consistent-field (MCSCF) framework which we shall call the coupled multiconfigurational (CMC) method. This technique, while similar to the CHF method, has several powerful advantages by virtue of its MCSCF 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) correlation effects may be included if desired.

As is common practice in CHF and other variational techniques, we employ the linear combination of atomic orbitals (LCAO)[16] scheme, utilizing Slater-type orbitals (STO's)[17] as basis functions, to solve the MCSCF equations in the CMC method. The normal procedure involves choosing a good Hartree-Fock atom basis and then augmenting it with a number of polarization functions. This immediately raises the problem of choosing proper basis functions for calculating the polarizability.

The polarization of an atom by an external field is, in effect, a distortion which is most prevalent at large distances from the atom in the tail of the wave function. Hence, the polarization functions must span this region in a sufficiently flexible manner in order to prevent any restrictions being imposed on the distortion process. Sitter and Hurst[5] have set forth rules for inclusion of the proper principal quantum number and spherical harmonic functions, but there appears to have been no systematic attempt to formulate rules for choosing exponents for the radial portions of these functions. Indeed, considering that the radial exponent determines the relative region of space spanned by the function, it is obvious that the polarizability should be sensitive to exponent variation of the polarization orbitals. Cohen[3] solved this problem in CHF calculations on helium and beryllium by simply optimizing the exponents of the polarization functions, but such a procedure can be costly when large numbers of functions are present.

The goal of the present paper is thus twofold: (a) to present the CMC formalism for calculating atomic polarizabilities of both degenerate and nondegenerate atoms, and (b) to develop rules for choosing a flexible set of exponents for the radial portions of the polarization functions. As an example, we report calculations on the ^1S, ^1D, and ^3P states of the neutral carbon atom, including a limited amount of correlation.

II. CMC METHOD

A. General

The theory and computational details of the MCSCF method have been adequately described elsewhere.[18] The calculations were performed with the BISON STO integral program[19] and the OVC (optimized valence configurations) MCSCF system[18] developed and made available to us by Wahl and Das of Argonne National Laboratories. To use the OVC program for the calculation of polarizabilities, we solve the equations for an atom in the presence of a finite field. For simplicity, this field is simulated with a charge particle[20] placed at varying distances from the atom. In this manner the OVC program was usable without requiring any modifications. Another attractive feature of this technique is that the distance between the charge and the atom may be varied inexpensively since the only basis-function integrals that change from point to point are the two-center, one-electron nuclear attraction terms. The other one-electron integrals and the two-electron integrals remain unchanged since all of the basis functions are centered on the atom.

The charge is placed at a distance R from, and along, the z axis of a coordinate system centered at the atom. The MCSCF equations for this system are then solved in $C_{\infty v}$ symmetry. For a given state of an atom, we use those configurations required to obtain the asymptotic HF state of the spherical atom, and then add any correlation configurations that are desired. We shall have more to say concerning the asymptotic behavior of $C_{\infty v}$ functions approaching the corresponding state of the spherical atom in a subsequent section.

B. Computation of Polarizability

It was stated in Sec. I that in CHF treatments the static polarizability could be expressed either as a function of the induced dipole moment or as a function of the second-order change in the energy. In this section, we derive the appropriate relationships used to obtain the polarizability in the CMC formalism.

Following Dalgarno,[15] let ψ_0 be the wave function for an N-electron system with Hamiltonian $\underline{\mathrm{H}}_0$, so that

$$(\underline{\mathrm{H}}_0 - E_0)\psi_0 = 0 \ . \tag{1}$$

In the presence of an electric field $\vec{\mathrm{F}}$ the perturbed wave function may be written as

$$\psi = \psi_0 + F\psi_1 \ , \tag{2}$$

where ψ_1 is the well-behaved solution of

$$(\underline{\mathrm{H}}_0 - E_0)\psi_1 + \underline{\mathrm{h}}\psi_0 = 0 \ , \tag{3}$$

with

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

In this framework, the static polarizability α is then a function of the second-order change in the energy of the atom as shown in Eq. (5):

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

For the case of the electric field being induced by a charge of magnitude Q', the perturbation may be expanded in a series of inverse powers of R as given by Eq. (6):

$$\underline{\mathrm{V}} = -Q'\sum_{i=1}^{N}\left[\frac{z_i}{R^2} + \frac{(3z_i^2 - r_i^2)}{2R^3} + \cdots O\left(\frac{1}{R^4}\right)\right] \ . \tag{6}$$

$\underline{\mathrm{V}}$ can be rewritten as

$$\underline{\mathrm{V}} = F\underline{\mathrm{h}}(R) \ , \tag{7}$$

where $F = Q'/R^2$ and

$$\underline{\mathrm{h}}(R) = -\sum_{i=1}^{N}\left[z_i + \frac{(3z_i^2 - r_i^2)}{2R} + \cdots O\left(\frac{1}{R^2}\right)\right] \ , \tag{8}$$

which renders it to a form consistent with the wave function defined by Eq. (2). Under these circumstances, the polarizability is field dependent and assumes the form

$$\alpha(R) = -2\langle\psi_0|\underline{\mathrm{h}}(R)|\psi_1\rangle \ . \tag{9}$$

The desired static polarizability comparable to that given by Dalgarno in Eq. (5) then becomes the limiting value of $\alpha(R)$ as the field strength approaches zero, or in the present case, as R approaches infinity, i.e.,

$$\alpha = \lim \alpha(R) \quad \text{as } R \to \infty \ . \tag{10}$$

Thus, in the CMC formalism, the MCSCF equations are solved for an atom in the presence of a perturbation given by Eq. (7), yielding a wave function of the form shown in Eq. (2) which will be hereafter referred to as Ψ_{CMC}.

It is now necessary to examine the means of obtaining the polarizability from Ψ_{CMC}. Consider the expectation value $\langle \Psi_{CMC} | \underline{z} | \Psi_{CMC} \rangle$. This may be expanded using Eq. (2) to give

$$\langle \Psi_{CMC} | \underline{z} | \Psi_{CMC} \rangle = \langle \psi_0 | \underline{z} | \psi_0 \rangle + 2F \langle \psi_0 | \underline{z} | \psi_1 \rangle + F^2 \langle \psi_1 | \underline{z} | \psi_1 \rangle , \quad (11)$$

where the first term and the leading member of the last term vanish because of the odd parity of $\underline{z}$. Thus,

$$\langle \psi_0 | \underline{z} | \psi_1 \rangle_{R \to \infty} = \frac{\langle \Psi_{CMC} | \underline{z} | \Psi_{CMC} \rangle}{2F} , \quad (12)$$

and this result may be substituted into Eq. (9) yielding

$$\alpha(R) = \frac{R^2}{Q'} \langle \Psi_{CMC} | \underline{z} | \Psi_{CMC} \rangle + \cdots O\left(\frac{1}{R^2}\right) . \quad (13)$$

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

C. Energy Relationships

The total energy of interaction for the charge-atom system may be written as

$$E_{CMC}(R) = \langle \Psi_{CMC} | \underline{H}_0 + F\underline{h}(R) | \Psi_{CMC} \rangle . \quad (14)$$

Expansion of Eq. (14) using Eqs. (2) and (6), with subsequent application of the interchange relation $\underline{H}_0\psi_1 = -\underline{h}\psi_0$ [from Eq. (3)], gives

$$E_{CMC}(R) = E_0 - \frac{Q'F}{R^2} \langle \psi_0 | \underline{z} | \psi_1 \rangle - \frac{Q'}{2R^3} \langle \psi_0 | 3\underline{z}^2 - \underline{r}^2 | \psi_0 \rangle - \frac{Q'F^2}{2R^3} \langle \psi_1 | 3\underline{z}^2 - \underline{r}^2 | \psi_1 \rangle - \cdots O\left(\frac{1}{R^4}\right) . \quad (15)$$

If one now makes use of the equality derived in Eq. (12), and a similar expansion and treatment for the expectation value $\langle \Psi_{CMC} | 3\underline{z}^2 - \underline{r}^2 | \Psi_{CMC} \rangle$, Eq. (15) becomes

$$\Delta E = -\frac{Q'}{2R^2} \langle \Psi_{CMC} | \underline{z} | \Psi_{CMC} \rangle - \frac{Q'}{2R^3} \langle \Psi_{CMC} | 3\underline{z}^2 - \underline{r}^2 | \Psi_{CMC} \rangle - \cdots O\left(\frac{1}{R^4}\right) , \quad (16)$$

where $\Delta E = E_{CMC} - E_0$. Finally, substitution of Eq. (13) into Eq. (16) gives

$$\alpha(R) = -\frac{2R^4}{Q'^2} \left[\Delta E + \frac{Q'}{2R^3} \langle \Psi_{CMC} | 3\underline{z}^2 - \underline{r}^2 | \Psi_{CMC} \rangle + \cdots O\left(\frac{1}{R^4}\right) \right] . \quad (17)$$

Thus, we have two formally equivalent routes to the polarizability based on quantities obtainable from the MCSCF wave function, one in terms only of the induced dipole moment [Eq. (13)] and the other in terms of the energy [Eq. (17)]. Also, Eq. (16) provides a useful self-consistent check between the computed energy of interaction and that based on the expansion of Eq. (8).

It should be pointed out that computing the polarizability from the induced dipole moment using Eq. (13) is preferable to obtaining it from the energy due to the unsatisfactory numerical uncertainties associated with manipulating the very large and very small numbers in Eq. (17). Cohen and Roothaan[2] reached a similar conclusion in their presentation of the CHF method.

In Sec. III, we present the results of CMC calculations of the dipole polarizabilities of the ^1S, ^1D, and ^3P states of the neutral carbon atom. The relations derived above will be examined in detail for these systems, particularly with regard to convergence as R approaches infinity.

III. APPLICATION TO CARBON

A. Choice of Basis Functions

The first step in using the CMC method for calculating the dipole polarizability of the carbon atom is the choice of proper basis functions. As mentioned in Sec. I, the polarizability is quite sensitive to the type of polarization functions augmenting the normal atomic basis. Sitter and Hurst[5] have recently reported rules for specifying the principal quantum number and spherical harmonic portions of the polarization orbitals, and while such rules are certainly valuable in that they determine the proper spherical harmonic and nodal structure for the polarization functions, they do not yield any specific information concerning the appropriate exponents for the radial terms. In CHF calculations on helium and beryllium, Cohen[3] variationally optimized the polarization-function exponents and found them to be considerably smaller than the unperturbed atomic-function exponents. This result is certainly reasonable since the distortion due to the field is largest in the tail of the wave function and hence should require relatively diffuse functions for a proper representation.

There are a number of possible ways to obtain an optimized set of polarization functions. First, one could simply choose the appropriate spherical harmonics as described above, and then variationally optimize the energy of the system with respect to the exponents of all the polarization functions as did Cohen. For small sets of functions as in helium or beryllium, this is not a particularly time-consuming process, but for larger atoms it could become quite expensive in terms of computer time. A second alternative would be to add several polarization functions of given principal quantum number and spherical harmonic, with exponents chosen so as to adequately span the entire region of space occupied by the wave function without generating linear dependencies. The variation method would then be allowed to choose which functions it would use most heavily to properly represent the distortion due to the field. The third, and most desirable, method would be to derive a relation to specify the polarization-function exponents solely from examination of the unperturbed atomic basis set.

In terms of time and computational expense, the second method described above is probably the most efficient route to generating a completely flexible set of polarization functions. The majority of the integrals are of the one-center variety for which rapidly executable analytic formulas exist. However, one of the ultimate goals of the present work is the determination of basis sets applicable to the study of van der Waals forces, hence we desire to keep the basis set as small as possible without sacrificing any significant flexibility in the ability of the polarization functions to handle the field-induced distortion in the wave function. It would thus be advantageous to develop a semiquantitative prescription to specify optimum exponents for a relatively small number of polarization functions without having to resort to brute-force exponent-optimization procedures.

Such a technique can be derived by considering Dalgarno and Parkinson's polarizability calculations[15] within the Hartree self-consistent-field approximation. Following the formal definitions given by Eqs. (1)–(5), they arrive at a solution which requires minimizing the one-electron functional

$$\epsilon_2=\langle u_i^{(1)}|\underline{\mathrm{H}}_i-\epsilon_0^i|u_i^{(1)}\rangle+2\langle u_i^{(1)}|\underline{\mathrm{h}}_i|u_i^{(0)}\rangle\ , \qquad (18)$$

where

$$\underline{\mathrm{H}}_i=-\tfrac{1}{2}\nabla_i^{\,2}+V_i(r_i) \qquad (19)$$

and $\underline{\mathrm{h}}_i$ is the ith component of $\underline{\mathrm{h}}$ in Eq. (4). The function $u_i^{(0)}$ is the unperturbed solution of

$$(\underline{\mathrm{H}}_i-\epsilon_0^i)u_i^{(0)}=0 \qquad (20)$$

and the functions $u_i^{(1)}$ may be identified as the polarization functions employed in the perturbed wave function. By specifying functional forms for $u_i^{(0)}$ and $u_i^{(1)}$, Eq. (18) is easily evaluated and thus may be used to generate a set of polarization functions. Specifically, if exponential functions such as STO's are assigned to $u_i^{(0)}$ and $u_i^{(1)}$, then the exponent of the latter may be determined by simply minimizing ϵ_2 with respect to this exponent. To simplify the procedure further, we use Slater's averaged effective potential[17] for $V_i(r_i)$, i.e.,

$$V_i(r_i)=-\zeta_i^{(0)}/r_i+n^*(n^*-1)/r_i^2\ , \qquad (21)$$

rather than the true potential which includes the two-electron interaction terms. Cohen's optimized basis-set CHF polarizability calculations on helium and beryllium[3] provide an excellent test of this technique. His initial helium HF basis set has as its largest component a 1s STO with $\zeta=1.45$, which yielded an optimized polarization exponent for the 2p function of 0.971. Using Cohen's 1s function with $\zeta=1.45$ for $u_i^{(0)}$ in Eq. (18), we obtain a 2p exponent for $u_i^{(1)}$ of 1.07, which is within 10% of Cohen's value. Similarly, for beryllium, the CHF calculations using unperturbed 2s functions with exponents of 1.29 and 0.845 yielded optimized exponents for the 2p polarization functions of 0.991 and 0.620, respectively. Use of Eq. (18) produced exponents for the 2p functions of 0.88 and 0.58, again, very close to the numbers obtained by Cohen.

The attractive feature of this technique is that Eq. (18) is a one-electron function, which means that approximately optimum polarization-function exponents may be trivially generated one by one rather than by the normal simultaneous brute-force method. Of course, since Eq. (18) is based on a Hartree wave function, one cannot expect to obtain exponents that agree quantitatively with those obtained from the fully optimized HF treatments which include exchange. However, the test results for helium and beryllium indicate that this procedure is an efficient tool for obtaining semiquantitative estimates of the optimum polarization-function exponents with a substantial savings in time and effort compared to the brute-force variation techniques.

In actual practice then, we use Sitter and Hurst's[5] rules for specifying the proper principal quantum numbers and spherical harmonics of the polarization functions, followed by application of Eq. (18) to determine a set of near optimum exponents. For carbon, we must consider polarization of the 2s and 2p orbitals, which implies the inclusion of s-, p-, and d-type polarization functions. The unperturbed atomic HF basis set for carbon is given in Table I. The dominant functions for the 2s orbital are those 2s functions with exponents of 2.141 and 1.354, and for the 2p orbital, those 2p functions with exponents of 1.625 and 1.054. Application of Eq. (18) to the two 2s functions yields optimum exponents for the 2p polarization functions of 1.05 and 0.90. Since the HF basis set contains a sufficient number of 2p functions in this exponent range, no further addition of p-type polarization orbitals was judged to be necessary. Polarization of the 2p orbital requires 3s and 3d functions, which were determined to require exponents of 1.4 and 1.15 for the 3s function, and 1.2 and 0.85 for the 3d function. Noting the approximate nature of this exponent determination procedure, we included 3d functions to properly span the predicted optimum exponent range, and

TABLE I. Carbon basis functions.[a]

Unperturbed atomic functions[b]			Polarization functions		
n	l	Exponent	n	l	Exponent
1	0	9.055	3	0	1.300
1	0	5.025	3	2	3.000
2	0	2.141	3	2	2.400
2	0	1.354	3	2	1.800
3	0	6.081	3	2	1.200
2	1	6.827	3	2	0.700
2	1	2.779	4	3	1.625
2	1	1.625	4	3	1.054
2	1	1.054			

[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. 19.

also added several additional $3d$ functions to ensure sufficient flexibility. The final set of polarization functions for carbon is listed in Table I. This basis was tested against a smaller set of polarization functions possessing only three $3d$ functions and no $3s$ function. The small 5–7% increase in polarizability observed for the larger basis was attributable almost completely to the lack of a $3s$ in the smaller set. Examination of the polarized wave function indicated that further augmentation of the basis would produce at most a 1–2% increase in the polarizability.

B. Asymptotic Considerations

As pointed out in Sec. II, our basic computational scheme consists of solving the MCSCF equations for the $C_{\infty v}$ charge-atom system using those configurations necessary to produce the asymptotic HF state of the atom (base configurations), and then any correlation configurations as desired. In the limit of a vanishing field as R approaches infinity, a region of discontinuity is encountered on passing from the $C_{\infty v}$ atom to the spherical atom, and it is appropriate at this point to examine the situation.

For carbon, the spherical ^1S, ^1D, and ^3P states project into several $C_{\infty v}$ states as given in Table II. The question that immediately arises is whether the solutions for the spherical and corresponding cylindrical states are formally equivalent, and if not, what manifestations are observed. In the solution of the SCF equations for either a spherical or $C_{\infty v}$ species, the basic procedure involves specifying an initial set of configurations, vectors, occupancies, and coupling schemes which in turn are used to generate an effective potential with which to start the iterative process. For the spherical atom, this potential is spherically averaged, whereas in the $C_{\infty v}$ case it is not (i.e., the potentials for electrons in degenerate atomic orbitals are not constrained to be equivalent but rather are separated into $\sigma, \pi, \delta, \ldots$ components). These initially generated potentials determine the eventual formal solution of the SCF equations, and hence there is no reason to expect the cylindrical and spherical treatments to be in perfect agreement.

The manifestations of this situation for the carbon atom may be determined by considering the energy expressions for the various asymptotes. Following Roothaan,[21] the energy of an open-shell species can be divided into three portions; that due only to closed shells, E_c; that due only to open shells, E_o; and that due to the interaction between the closed and open shells, E_{co}. Thus,

$$E = E_c + E_o + E_{co} \quad , \tag{22}$$

where

$$E_c = 2\sum_k H_k + \sum_{k,l} (2J_{kl} - K_{kl}) \quad , \tag{23}$$

$$E_o = f[2\sum_m H_m + f \sum_{m,n} (2aJ_{mn} - bK_{mn})] \quad , \tag{24}$$

$$E_{co} = 2 \sum_{k,m} (2J_{km} - K_{km}) \quad , \tag{25}$$

and the constants $a, b,$ and f depend on the specific case. The running indices over k and l are for closed shells, m and n are for open shells, and H_i, J_{ij}, and K_{ij} are the normal one-electron, Coulomb, and exchange integrals, respectively. Inspection of Eqs. (22)–(25) reveals that E_c and E_{co} will be equivalent for both the $C_{\infty v}$ and spherical cases if the corresponding orbitals are the same. Any formal difference will thus occur in E_o. Using Roothaan's tables for the a, b, and f constants, we can derive the open-shell energy of the ^3P spherical carbon atom to be

$$E_o(^3P) = 2H_{2p(1)} + J_{2p(1),2p(-1)} - K_{2p(1),2p(-1)} , \tag{26}$$

where the subscripts indicate the $2p$ vector with the m_l quantum number in parentheses. Similarly, the energy of the corresponding $^3\Sigma^-$ and $^3\Pi$ cylindrical states may be obtained as

$$E_o(^3\Sigma^-) = E_o(^3\Pi) = 2H_{2p\pi} + J_{2p\pi, 2p\bar{\pi}} - K_{2p\pi, 2p\bar{\pi}} . \tag{27}$$

Comparing Eqs. (26) and (27), we find that the solutions for the $^3\Sigma^-$ and $^3\Pi$ states are formally equal to that of the ^3P asymptote providing the corresponding orbitals are equivalent. On the other hand, the ^1D open-shell energy can be derived

TABLE II. Carbon asymptotic states.

Spherical	$C_{\infty v}$
^1S	$^1\Sigma^+$
^1D	$^1\Sigma^+$, $^1\Pi$, $^1\Delta$
^3P	$^3\Sigma^-$, $^3\Pi$

TABLE III. Carbon base configurations.[a]

State	Configurations
$^1\Sigma^+$ (^1S)	$1\sigma^2 2\sigma^2 3\sigma^2(^1\Sigma^+\times\,^1\Sigma^+) + 1\sigma^2 2\sigma^2 1\pi^2(^1\Sigma^+\times\,^1\Sigma^+)$ [b]
$^1\Sigma^+$ (^1D)	$1\sigma^2 2\sigma^2 3\sigma^2(^1\Sigma^+\times\,^1\Sigma^+) + 1\sigma^2 2\sigma^2 1\pi^2(^1\Sigma^+\times\,^1\Sigma^+)$ [c]
$^1\Delta$ (^1D)	$1\sigma^2 2\sigma^2 1\pi^2(^1\Sigma^+\times\,^1\Delta)$
$^1\Pi$ (^1D)	$1\sigma^2 2\sigma^2 3\sigma 1\pi(^1\Sigma^+\times\,^1\Pi)$
$^3\Sigma^-$ (^3P)	$1\sigma^2 2\sigma^2 1\pi^2(^1\Sigma^+\times\,^3\Sigma^-)$
$^3\Pi$ (^3P)	$1\sigma^2 2\sigma^2 3\sigma 1\pi(^1\Sigma^+\times\,^3\Pi)$

[a]Quantities in parentheses indicate coupling scheme for the four valence electrons taken two at a time.

[b]MCSCF calculation performed by minimizing energy of the second CI root.

[c]MCSCF calculation performed by minimizing energy of the lowest CI root.

to be

$$E_o(^1D) = 2H_{2p(1)} + 0.4J_{2p(1),2p(1)} + 0.6J_{2p(1),2p(-1)} + 0.2K_{2p(1),2p(-1)}\,. \quad (28)$$

The corresponding expression for the $^1\Delta$ $C_{\infty v}$ state is

$$E_o(^1\Delta) = 2H_{2p\pi} + 0.5J_{2p\pi,2\pi p} + 0.5J_{2p\pi,2p\bar{\pi}}\,. \quad (29)$$

Clearly, Eqs. (28) and (29) are not the same, indicating that the formal solution for the $^1\Delta$ state is not equivalent to its ^1D asymptote. Analogous equations can be derived for the other cylindrical states, and one finds that the $^1\Sigma^+$ state originating from the ^1S asymptote and the $^3\Sigma^-$ and $^3\Pi$ states originating from the ^3P asymptote have solutions that are formally equivalent to that of their spherical analog, whereas the $^1\Sigma^+$, $^1\Delta$, and $^1\Pi$ states coming from the ^1D asymptote do not.

To illustrate this effect, we have tabulated in Table IV the computed energies for the $C_{\infty v}$ and spherical carbon asymptotes using the basis set given in Table I and the base configurations for the molecular states as presented in Table III. It is immediately obvious that the conclusions derived above are borne out by the results in Table IV, except that even the $^1\Sigma^+(^1S)$, $^3\Sigma^-$, and $^3\Pi$ state energies do not agree exactly with their corresponding spherical asymptotes. This is due to higher-quantum-number functions included in the basis set, which are allowed to mix in the molecular calculations, but are symmetry forbidden in the spherical case. On passing from spherical to cylindrical symmetry, even-parity (with respect to the spherical atomic symmetry) functions are allowed to mix with the original atomic functions. This effect is illustrated in Table V, where we have tabulated the 2σ ($2s$) vectors for the $^3\Sigma^-$ and $^3\Pi$ cases compared to those of the ^3P spherical species. Note that the $3d$ functions have been mixed with the $2s$ functions in both of the cylindrical vectors. A similar situation occurs in the $2p\sigma$ and $2p\pi$ vectors, where the $4f$ functions are mixed with the unperturbed atomic $2p$ functions. This mixture of higher functions into the vectors should account for the small discrepancies between the $^3\Sigma^-$ and $^3\Pi$ energies and that of the ^3P energy. Considering that such a mixture of even-parity functions will produce a second-order quadrupolar effect in the energy, and that the ratio of the quadrupole tensors for Σ and Π components is $-2:1$, then we would expect the energy lowering to be the square of this ratio, or 4:1. The energy differences given in Table IV for the $^3\Sigma^-$ and $^3\Pi$ states relative to the ^3P certainly support this postulate. Also, one observed in Table V that the coefficients of the $3d$ functions in the $2s$ vectors of these states are in the ratio $-2:1$.

In the preceding discussion, we have attempted to point out the possible discontinuities which may arise when a degenerate atom passes from spherical to cylindrical symmetry. For the carbon atom, it has been shown that certain of the $C_{\infty v}$ states have equivalent formal solutions with their asymptotes, whereas others do not. It should be recognized that these equivalences are merely circumstantial and are due entirely to coupling

TABLE IV. Comparison of $C_{\infty v}$ and spherical asymptotic energies for carbon.

$C_{\infty v}$		Spherical		
State	Energy	State	Energy	Δ[a]
$^1\Sigma^+$	$-37.548\,902$	^1S	$-37.548\,901$	$-0.000\,001$
$^1\Sigma^+$	$-37.634\,815$	^1D	$-37.631\,258$	$-0.003\,557$
$^1\Delta$	$-37.631\,501$	^1D	$-37.631\,258$	$-0.000\,243$
$^1\Pi$	$-37.633\,143$	^1D	$-37.631\,258$	$-0.001\,885$
$^3\Sigma^-$	$-37.688\,680$	^3P	$-37.688\,620$	$-0.000\,060$
$^3\Pi$	$-37.688\,632$	^3P	$-37.688\,620$	$-0.000\,012$

[a]$\Delta \equiv C_{\infty v}$ energy minus spherical energy.

TABLE V. Comparison of $C_{\infty v}$ and spherical asymptotic $2s$ vectors for carbon.

Function	Exponent	$^3\Sigma^-$	$^3\pi$	^3P
$1s$	9.055	$-0.003\,30$	$-0.003\,30$	$-0.003\,30$
$1s$	5.025	$-0.254\,12$	$-0.254\,12$	$-0.254\,12$
$2s$	2.141	0.492 76	0.492 76	0.492 76
$2s$	1.354	0.598 25	0.598 18	0.598 18
$3s$	1.300	0.000 10	0.000 18	0.000 20
$3s$	6.081	$-0.030\,21$	$-0.030\,21$	$-0.030\,21$
$2p$	6.827	0.0	0.0	0.0
$2p$	2.779	0.0	0.0	0.0
$2p$	1.625	0.0	0.0	0.0
$2p$	1.054	0.0	0.0	0.0
$3d$	3.000	$-0.007\,35$	0.003 65	0.0
$3d$	2.400	0.012 88	$-0.006\,42$	0.0
$3d$	1.800	$-0.007\,48$	0.003 79	0.0
$3d$	1.200	$-0.003\,73$	0.001 67	0.0
$3d$	0.700	$-0.000\,11$	0.000 06	0.0
$4f$	1.625	0.0	0.0	0.0
$4f$	1.054	0.0	0.0	0.0

TABLE VI. CMC polarizability and energy results for carbon.[a]

State	R	$\langle z\rangle$	$\langle 3z^2-r^2\rangle$	$\alpha(\langle z\rangle)$[b]	$\alpha(\Delta E)$[c]	E_{SCF}	ΔE_{SCF}[d]	$\Delta E'$[e]
$^1\Sigma^+$ (^1S)	12	0.08590	−0.08401	12.37	13.07	−37.549193	−0.00029	−0.00028
	15	0.05486	−0.03329	12.35	12.65	−37.549022	−0.00012	−0.00012
	18	0.03796	−0.01641	12.31	12.48	−37.548959	−0.00006	−0.00006
$^1\Sigma^+$ (^1D)	12	0.09505	3.48025	13.69	12.36	−37.636119	−0.00131	−0.00133
	15	0.06004	3.35625	13.50	12.91	−37.635436	−0.00062	−0.00063
	18	0.04136	3.30083	13.40	12.80	−37.635159	−0.00034	−0.00034
$^1\Delta$(^1D)	12	0.07378	−3.13601	10.62	9.93	−37.630833	0.00067	0.00066
	15	0.04716	−3.16363	10.61	10.41	−37.631132	0.00037	0.00037
	18	0.03269	−3.17847	10.59	10.39	−37.631277	0.00022	0.00022
$^1\Pi$(^1D)	12	0.08554	1.70333	12.32	11.87	−37.633921	−0.00078	−0.00079
	15	0.05424	1.65393	12.20	11.94	−37.633505	−0.00036	−0.00037
	18	0.03742	1.63126	12.12	12.00	−37.633340	−0.00020	−0.00020
$^3\Sigma^-$(^3P)	12	0.06985	−3.02985	10.08	9.82	−37.688041	0.00064	0.00064
	15	0.04466	−3.05461	10.06	10.39	−37.688331	0.00035	0.00035
	18	0.03109	−3.06546	10.06	10.30	−37.688471	0.00021	0.00021
$^3\Pi$(^3P)	12	0.09007	1.62364	12.97	12.49	−37.689403	−0.00077	−0.00078
	15	0.05723	1.57997	12.88	12.65	−37.688990	−0.00036	−0.00036
	18	0.03918	1.56199	12.70	12.61	−37.688826	−0.00019	−0.00019

[a]Results obtained using base configurations given in Table III. All numbers in atomic units.
[b]Calculated using Eq. (13).
[c]Calculated using Eq. (17).
[d]Calculated by subtracting cylindrical energy E_0 as given in Table IV from corresponding E_{SCF}.
[e]Calculated using Eq. (16).

schemes which happen to generate potentials which are the same as the spherically averaged potential of the asymptote.

The most important point to be realized from this analysis is simply recognition of the situation. In the calculation of atomic polarizabilities from the induced moment, the manifestations of the discontinuities are not important since the field induces dominantly odd-parity transitions with respect to the unperturbed atomic functions at large R, whereas the symmetry reduction to $C_{\infty v}$ involves only even-parity mixings, which result in no net dipole moment. However, if the polarizabilities are calculated from the second-order energy of interaction by Eq. (17), then the effect must be taken into consideration. Hence, for the results presented in Sec. II C, we use the $C_{\infty v}$ asymptotes for E_0 in Eqs. (16) and (17). As will become evident, use of the spherical quantities would have produced large and unacceptable discrepancies in the results.

C. Base Configuration Results for Carbon

As an initial test of the CMC method, we calculated polarizabilities for all of the states originating from the ^1S, ^1D, and ^3P asymptotes of carbon using only the base configurations listed in Table III. The results are presented in Table VI. The polarizabilities were calculated in two ways: (i) from the induced dipole moment at the carbon, $\langle z\rangle$ [Eq. (13)], and (ii) from the calculated energy of interaction ΔE_{SCF} [Eq. (17)]. The agreement between the polarizabilities from the two formulas is good; however, it is obvious that the values obtained from the induced moment are more consistent and exhibit less scatter than those obtained from the energy. As pointed out previously, such behavior of the energy quantities is due to the inherent numerical uncertainties associated with Eq. (17). The polarizabilities computed from the induced moment are considerably more stable as a function of R than those based on the energy, but we should point out that they are not of sufficient accuracy to allow the extraction of higher-order effects such as hyperpolarizabilities and shielding factors. Cohen[3] likewise found his relatively small basis-set results for the beryllium series to be of insufficient accuracy to obtain reliable estimates of these quantities. This situation is not surprising in light of Sitter and Hurst's results and discussion[5] which indicate that a much larger basis set than that employed by us would be necessary to obtain reasonable estimates of these quantities.

To test the self-consistency and convergence properties of the calculations, we have computed and listed in Table VI the energy of interaction of the field with the atom by two independent methods: (a) from the difference between the calculated MCSCF total energy and the energy of the cylindrical asymptote, which is designated ΔE_{SCF}, and (b) from the expectation values of the dipole

TABLE VII. Carbon ($^1\Pi$)$2s(\sigma)$ vectors.

Function	Exponent	$R=12$ a.u.	$R=15$ a.u.	$R=18$ a.u.	$R=\infty$
$1s$	9.055	−0.003 25	−0.003 25	−0.003 25	−0.003 25
$1s$	5.025	−0.255 70	−0.255 69	−0.255 69	−0.255 71
$2s$	2.141	0.501 24	0.500 96	0.500 84	0.500 75
$2s$	1.354	0.593 57	0.594 07	0.594 26	0.594 52
$3s$	1.300	−0.003 43	−0.003 65	−0.003 73	−0.003 92
$3s$	6.081	−0.030 90	−0.030 87	−0.030 87	−0.030 85
$2p$	6.827	−0.000 01	−0.000 01	0.0	0.0
$2p$	2.779	0.002 87	0.001 82	0.001 28	0.0
$2p$	1.625	−0.003 34	−0.002 07	−0.001 39	0.0
$2p$	1.054	0.014 64	0.009 33	0.006 51	0.0
$3d$	3.000	0.003 28	0.003 42	0.003 47	0.003 55
$3d$	2.400	−0.005 11	−0.005 63	−0.005 82	−0.006 10
$3d$	1.800	0.001 62	0.002 45	0.002 81	0.003 27
$3d$	1.200	0.004 42	0.003 37	0.002 91	0.002 30
$3d$	0.700	0.000 32	0.000 16	0.000 11	0.000 04
$4f$	1.625	−0.000 16	−0.000 08	−0.000 05	0.0
$4f$	1.054	0.000 51	0.000 23	0.000 13	0.0

and quadrupole operators as given in Eq. (16), which are designated $\Delta E'$. As can be seen in Table VI, the agreement between ΔE_{SCF} and $\Delta E'$ is excellent, particularly at large R, where the two sets of figures are nearly identical. Not only does such a result justify the neglect of higher-order terms in Eq. (8), but it also establishes the numerical accuracy and reliability of the CMC method. Noting the magnitudes of these interaction energies, it becomes apparent that use of the spherical-atom results for E_0 rather than the cylindrical quantities would have led to large discrepancies between ΔE_{SCF} and $\Delta E'$. In fact, it is evident in Table IV that the differences between the energies of the cylindrical and spherical asymptotes are, in certain cases, orders of magnitude greater than the corresponding ΔE values in Table VI.

To illustrate the actual distortion on the wave function due to the field, we have tabulated the $2s(\sigma)$, $2p(\sigma)$ and $2p(\pi)$ vectors for the $^1\Pi$ state as a function of distance in Tables VII–IX. For each vector, the coefficients of the polarization functions increase with increasing field strength (decreasing R) as expected. The $2s$ vector is polarized by the $2p$ functions, and the $2p$ vectors are polarized by the $3s$ and $3d$ functions. One gratifying feature observed for these vectors is that where the variation principle was given a choice of polarization functions it always selected as the dominant term the functions with exponents nearly equal to those predicted to be optimum from application

TABLE VIII. Carbon ($^1\Pi$)$2p(\sigma)$ vectors.

Function	Exponent	$R=12$ a.u.	$R=15$ a.u.	$R=18$ a.u.	$R=\infty$
$1s$	9.055	−0.000 03	−0.000 12	−0.000 01	0.0
$1s$	5.025	0.005 48	0.003 50	0.002 45	0.0
$2s$	2.141	0.013 06	0.008 15	0.005 54	0.0
$2s$	1.354	−0.065 55	−0.041 49	−0.028 69	0.0
$3s$	1.300	0.048 29	0.030 58	0.021 09	0.0
$3s$	6.081	−0.001 30	−0.000 81	−0.000 55	0.0
$2p$	6.827	0.006 98	0.007 07	0.007 12	0.007 16
$2p$	2.779	0.192 06	0.191 28	0.190 95	0.190 56
$2p$	1.625	0.359 64	0.364 33	0.366 69	0.368 16
$2p$	1.054	0.517 94	0.513 88	0.511 74	0.510 60
$3d$	3.000	−0.001 60	−0.001 04	−0.000 72	0.0
$3d$	2.400	0.005 77	0.003 76	0.002 61	0.0
$3d$	1.800	−0.011 35	−0.007 45	−0.005 19	0.0
$3d$	1.200	0.011 40	0.007 53	0.005 30	0.0
$3d$	0.700	0.007 12	0.003 96	0.002 56	0.0
$4f$	1.625	0.024 90	0.025 42	0.025 59	0.025 80
$4f$	1.054	−0.005 27	−0.007 16	−0.007 89	−0.008 80

TABLE IX. Carbon ($^1\Pi$)$2p(\pi)$ vectors.

Function	Exponent	R=12 a.u.	R=15 a.u.	R=18 a.u.	$R=\infty$
$2p$	6.827	0.007 22	0.007 19	0.007 17	0.007 14
$2p$	2.779	0.190 32	0.190 45	0.190 68	0.190 84
$2p$	1.625	0.372 58	0.370 85	0.369 53	0.368 11
$2p$	1.054	0.505 86	0.507 58	0.508 78	0.510 13
$3d$	3.000	−0.002 06	−0.001 27	−0.000 92	0.0
$3d$	2.400	0.006 71	0.004 22	0.003 00	0.0
$3d$	1.800	−0.006 31	−0.004 05	−0.002 81	0.0
$3d$	1.200	0.008 87	0.005 77	0.003 95	0.0
$3d$	0.700	0.004 44	0.003 00	0.002 13	0.0
$4f$	1.625	−0.040 99	−0.040 76	−0.040 74	−0.040 63
$4f$	1.054	0.016 34	0.015 33	0.014 90	0.014 28

of Eq. (13). For example, the $2s$ vector is polarized most heavily by the $2p$ function with an exponent of 1.054, which is virtually in perfect agreement with that predicted in Sec. III A. This result further demonstrates the reliability of our simplified method of determining polarization-function exponents.

D. Correlation Results

For the first-row atoms, it is well established that a significant portion of the correlation effects may be handled by considering the correlation from the valence shell[22] and the most important portions of the "semi-internal" correlations[23] which correspond to terms involving single excitations to orbitals outside of the valence shell.

For the purpose of performing an initial exploration of the effect of correlation on the polarizability and to illustrate the ease with which correlation may be handled by the CMC method, we have calculated polarizabilities for the various states of the carbon atom including the valence-shell correlation terms corresponding to $2s^2 2p^2 \rightarrow 2p^4$ double excitations. The results are given in Table X compared to the base-configuration results. As anticipated, the correlated polarizabilities decreased between 5 and 10% relative to the base results which is consistent with a slight contraction of the valence orbitals due to the correlation.

There are, of course, other correlation configurations for the carbon atom which have been omitted in the present treatment. The $2p^4$ terms were included only to illustrate the versatility of the CMC method. A more complete analysis of the effect of correlation on polarizabilities is forthcoming.

TABLE X. Correlated polarizability results for carbon.[a]

State	Polarizability Base[b]	Correlated[c]
$^1\Sigma^+(^1S)$	1.82	1.77
$^1\Sigma^+(^1D)$	1.98	1.93
$^1\Delta(^1D)$	1.57	1.51
$^1\Pi(^1D)$	1.79	1.76
$^3\Sigma^-(^3P)$	1.49	1.42
$^3\Pi(^3P)$	1.88	1.78

[a]Values in Å^3.
[b]Calculated using only base configurations given in Table III.
[c]Calculated using base configurations plus $s^2p^2 \rightarrow p^4$ correlation configurations.

E. Comparison with Other Results

Miller and Kelly[13] have recently reported MBPT calculations on the dipole polarizability of the carbon atom in its ^3P ground state. Their results are compared to our final correlation figures for the $M_L=0$ ($^3\Sigma^-$) and $M_L=\pm 1$ ($^3\Pi$) states in Table XI. The final value for the ^3P state is given by the weighted average of these two components, and these figures are also given in Table XI. The MBPT and CMC polarizabilities agree to 10% which is within the uncertainty Kelly ascribes to his values; however, a direct comparison with the MBPT results is somewhat artificial in that it is very difficult to establish corresponding levels of equivalence between the two methods. Certainly in the limit that the MBPT treatment is correctly carried to infinite order in both the correlation and the field, the results should agree with CMC calculations including all of the dominant correlation terms. Caves and Karplus[8] have compared MBPT to the CHFP method in detail, and the reader is referred to this paper for an excellent analysis of the two techniques, the latter

TABLE XI. Comparison of CMC and MBPT results.[a]

State	α(MBPT)[b]	α(CMC)
$^3\Sigma^-$ ($M_L=0$)	1.44	1.42
$^3\Pi$ ($M_L=\pm 1$)	1.59	1.78
^3P (averaged)	1.54	1.66

[a]Values in Å^3.
[b]MBPT results taken from Ref. 13.

of which is equivalent to the CMC method in the limit of a vanishing field and use of only a reference HF configuration.

Our final dipole polarizabilities averaged over M_L components for the ^1S, ^1D, and ^3P states of the carbon atom are 1.77, 1.68, and 1.66 Å^3, respectively, to which we ascribe uncertainties of 5–10% due mainly to the lack of including all of the correlation configurations. Dalgarno and Parkinson[15] using the Hartree approximation with partial inclusion of exchange effects calculated the polarizability of carbon to be 2.1 Å^3 for the ^3P state which is significantly larger than our figure and Kelly's value. The only other available figure is due to Thorhallsson, Fisk, and Fraga,[24] who calculate a value of 1.75 Å^3 for the ^3P state from an approximate uncoupled HF theory using available SCF wave functions.

IV. SUMMARY AND DISCUSSION

In summary, we have described the CMC method for calculating dipole polarizabilities of atoms and applied it to the ground state of the neutral carbon atom. While this technique is similar to the CHF method, and, in the limit of a vanishing field, to the CHFP method, it possesses several powerful advantages by virtue of its MCSCF formalism, including (i) straightforward applicability to any state, including excited states, of both degenerate and nondegenerate atoms, and (ii) explicit introduction of correlation effects to any degree desired. The reported calculations on carbon were correlated with only the dominant $2p^4$ terms to illustrate the flexibility of the CMC method, and the estimated uncertainties (5–10%) in the calculated polarizabilities reflect the omission of other less-important correlation configurations. The results are in good agreement with the ^3P ground-state results obtained by Miller and Kelly[13] using MBPT, which is probably the most reliable of the other theoretical calculations of the dipole polarizability of carbon. To our knowledge, no experimental figures are available for comparison.

The basis machinery for CMC polarizability calculations is straightforwardly applicable to most atoms. The most important variable is the choice of a proper set of polarization functions. Using Sitter and Hurst's[5] rules for selecting the appropriate principal quantum number and spherical-harmonic functions, we have shown that the simple minimization of a one-electron function derived from the Hartree approximation provides the means for specifying a flexible set of exponents for these functions.

Thus, the CMC method has been demonstrated to be an efficient and versatile tool for the calculation of atomic polarizabilities. In a future publication, CMC calculations on the dipole polarizabilities of the other first-row atoms will be presented.

ACKNOWLEDGMENTS

We are happy to thank Dr. Frederick H. Mies, Dr. Arnold C. Wahl, and Dr. Walter J. Stevens for many helpful discussions, and Dr. David B. Neumann for his help in the computational aspects of the work. We are indebted to Dr. A. C. Wahl and Dr. G. Das for making available the BISON integral program and the OVC (optimized valence configurations) MCSCF program, which made possible the calculations reported in this paper. Part of the computations were performed at Goddard Space Center, NASA, through the cooperation of Dr. B. Donn of the Astrochemistry Section at NASA.

---

*NRC-NBS Postdoctoral Associate 1971–1972.

†This work was supported in part by NASA.

[1]See R. R. Teachout and R. T. Pack [Atomic Data 3, 195 (1971)] for an excellent review of available theoretical and experimental data on the static dipole polarizabilities of neutral atoms.

[2]H. D. Cohen and C. C. J. Roothaan, J. Chem. Phys. 43, 534 (1965).

[3]H. D. Cohen, J. Chem. Phys. 43, 3558 (1965).

[4]J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, J. Chem. Phys. 49, 2960 (1968).

[5]R. E. Sitter, Jr. and R. P. Hurst, Phys. Rev. A 5, 5 (1972).

[6]A. Dalgarno, Advan. Phys. 11, 281 (1962).

[7]P. W. Langhoff, M. Karplus, and R. P. Hurst, J. Chem. Phys. 44, 505 (1966).

[8]T. C. Caves and M. Karplus, J. Chem. Phys. 50, 3649 (1969).

[9]S. T. Epstein and R. E. Johnson, J. Chem. Phys. 47, 2275 (1967).

[10]D. F. Tuan, S. T. Epstein, and J. O. Hirschfelder, J. Chem. Phys. 44, 431 (1966).

[11]J. I. Musher, J. Chem. Phys. 46, 369 (1967).

[12]H. P. Kelly, Phys. Rev. 152, 62 (1966).

[13]J. H. Miller and H. P. Kelly, Phys. Rev. A 5, 516 (1972).

[14]E. S. Chang, R. T. Pu, and T. P. Das, Phys. Rev. 174, 16 (1968).

[15]A. Dalgarno and D. Parkinson, Proc. Roy. Soc. (London) A250, 422 (1959).

[16]C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[17]J. C. Slater, Phys. Rev. 36, 57 (1930).

[18]A. C. Wahl and G. Das, Advan. Quantum Chem. 5, 261 (1970); G. Das and A. C. Wahl, J. Chem. Phys. 56, 1769 (1972). The MCSCF program used to perform the calculations is the OVC (optimized valence configurations) program written by G. Das, A. C. Wahl, and K. Kaiser of the Argonne National Laboratory, Argonne, Ill.

[19]A. C. Wahl, P. J. Bertoncini, K. Kaiser, and R. H.

Land, Argonne National Laboratory Report No. ANL-7271, 1968 (unpublished).

[20] A. D. McLean and M. Yoshimine, J. Chem. Phys. 46, 3682 (1967).

[21] C. C. J. Roothaan, Rev. Mod. Phys. 32, 179 (1960).

[22] A. W. Weiss, Phys. Rev. 162, 71 (1967); 188, 119 (1969); Phys. Rev. A 3, 126 (1971).

[23] O. Sinanoğlu, *Advances in Chemical Physics* (Interscience, New York, 1969), Vol. 14, p. 237, and references cited therein.

[24] J. Thorhallsson, C. Fisk, and S. Fraga, Theoret. Chim. Acta 10, 388 (1968).

PHYSICAL REVIEW A VOLUME 6, NUMBER 3 SEPTEMBER 1972

Second-Order Corrections to the Fine Structure of Helium. II. Contributions from ^1P and ^3D Intermediate States*

Lars Hambro†

Department of Physics, University of California, San Diego, La Jolla, California 92037

(Received 20 March 1972)

The contributions from the three spin-dependent Breit operators in second-order perturbation theory are calculated when the symmetries of the intermediate states are odd ^1P or ^3D. Standard Hylleraas expansions with up to 165 terms are used for the perturbations of the wave functions. The large interval of the fine structure of the 2 ^3P level in helium is increased by $2.17(2)\times10^{-4}$ cm^{-1} by ^1P, and by $0.0089(6)\times10^{-4}$ cm^{-1} by ^3D. Two methods for handling angular integration over D tensors are described.

I. INTRODUCTION

In an earlier paper,[1] hereafter referred to as I, the contributions to the fine structure of the $2\,^3P$ level of helium from second-order perturbation theory with intermediate ^3P states were calculated. This fine structure consists of two intervals whose experimental values are $\nu_{12}=764.2606\,(17)$ cm^{-1} and $\nu_{01}=9879.121\,(12)$ cm^{-1}.[2] The relative accuracy of the large interval is thus better than for the small interval (1.2 ppm vs 2.2 ppm), and the results of I came much closer to the desired accuracy (which is to match the absolute experimental accuracy) for the large interval than for the small; so, in this paper the remaining second-order contributions to the large interval are calculated. These come from intermediate states with ^1P and ^3D symmetries. There are also contributions from ^1D and ^3F states to the small interval which have not yet been calculated. As in I, one solves an inhomogeneous Schrödinger equation for the odd ^1P and ^3D perturbations of the $2\,^3P$ wave function by the variational method; the second-order perturbation energies are then given by integrals. We emphasize that this is but one of many theoretical contributions to the fine structure. A summary of the complete calculation of the fine-structure intervals, including quantum-electrodynamic and nuclear-motion effects, with detailed comparison with experiment, will be reported.[3]

II. ^1P EXPANSION

The two spin-orbit operators which connect singlet and triplet states are ($Z=2$ for neutral helium)

$$\tilde{H}_1^{(1)}=\tfrac{1}{4}\alpha^2 Z\left(\frac{\vec{\sigma}_1-\vec{\sigma}_2}{2}\right)\cdot\left(\frac{\vec{r}_1\times\vec{p}_1}{r_1^3}-\frac{\vec{r}_2\times\vec{p}_2}{r_2^3}\right),$$

$$\tilde{H}_2^{(1)}=\tfrac{1}{4}\alpha^2\left(\frac{\vec{\sigma}_1-\vec{\sigma}_2}{2}\right)\cdot\left(\frac{\vec{r}_1-\vec{r}_2}{r_{12}^3}\times(\vec{p}_1+\vec{p}_2)\right),$$

which follow from the well-known operators with just one $\vec{\sigma}$.[4] The equation for the ^1P perturbation to the $2\,^3P$ wave function is

$$(H_0-E_0)\,\tilde{\Psi}_1^{(i)}(^1P_1)=-\tilde{H}_1^{(i)}\,\Psi_0(^3P_1)\,,\quad i=1,2 \tag{1}$$

which differs from the basic equation [Eq. (6) of Paper I] because the expectation value of $\tilde{H}_1^{(i)}$ is zero in a state of definite multiplicity. H_0 is the nonrelativistic Hamiltonian in atomic units:

$$H_0=-\tfrac{1}{2}\nabla_1^2-\tfrac{1}{2}\nabla_2^2-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_{12}}\,.$$

The unperturbed wave function with total angular momentum $J=1$ and $M_J=1$ is

$$\Psi_0(^3P_1,M_J=1)=\sum_{l,m,n=0}^{l+m,n\leq\omega'}C_{lmn}U_{lmn}(^3P_1,M_J=1)\,, \tag{2}$$

where

$$U_{lmn}(^3P_1,M_J=1)=\frac{1-P_{12}}{4\pi\sqrt{2}}\left(S_0^{(1)}\{\vec{r}_1\}^{(1)}-S_1^{(1)}\{\vec{r}_1\}_0^{(1)}\right)u_{lmn}(1,2)\,,$$

P_{12} exchanges coordinates $\vec{r}_1$ and $\vec{r}_2$,

$$u_{lmn}(1,2)=r_{12}^{\,l}r_1^{\,m}r_2^{\,n}e^{-(\kappa\sigma/2)r_1}e^{-(\kappa/2)r_2}$$

as in I ($\kappa=4.62$ and $\sigma=0.29$), and