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Many-Body Perturbation-Theory Calculation of Atomic Polarizabilities*

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The use of many-body perturbation theory in problems involving multiple perturbations is discussed. The perturbation theory is applied to the calculation of the dipole polarizability of the ground state and of a number of low-lying excited states for atomic oxygen. For the ^3P ground state, the calculated polarizability is 0.783×10^{-24} cm.^{3} The effects of electron correlations are discussed. The monopole and dipole contributions to the polarization potential are presented for the $(2p)^3\,{}^4S\,3s\,{}^5S$ state.

I. INTRODUCTION

THE many-body perturbation theory of Brueckner[1] and Goldstone[2] has previously been applied to calculations of many atomic properties. Results have been obtained for correlation energies,[3] dipole and quadrupole polarizabilities,[4] shielding factors, transition probabilities, and photoionization cross sections for the neutral beryllium atom.[5] Recent research has also shown that the Brueckner-Goldstone (BG) perturbation expansion may be applied to open-shell atoms, and correlation energies among all electron pairs in the neutral oxygen atom have been obtained.[6]

In this paper the BG expansion is used to calculate the dipole polarizability for the ground state and for the low-lying excited states of the neutral oxygen atom. For the ground-state calculation, the effects of correlation terms are considered. Calculations are also given for the polarizability potential for the $(2p)^3\,{}^4S\text{-}{}^5S$ excited state of oxygen. A review of the BG theory and its applicability to problems involving multiple perturbations is given in Sec. II. The dipole polarizability calculations are reported in Sec. III and the polarization potential calculations are reported in Sec. IV. Section V contains the discussion and conclusions.

II. PERTURBATION THEORY

A. Review of the Brueckner-Goldstone Expansion

The total Hamiltonian for N identical fermions interacting through two-body potentials v_{ij} is

$$H=\sum_{i=1}^{N} T_i+\sum_{i<j}^{N} v_{ij}. \tag{1}$$

The term T_i is the sum of the kinetic-energy operator and all one-body potentials for the ith fermion. For atoms

$$T_i=-(\hbar^2/2m)\nabla_i^2-Ze^2/r_i, \tag{2}$$

where Ze is the nuclear charge. The states ψ_n are defined by

$$H\psi_n=E_n\psi_n. \tag{3}$$

The effect of the N interacting fermions may be approximated by a single-particle potential V and ψ_n is now approximated by Φ_n, where

$$H_0\Phi_n=E_n^{(0)}\Phi_n \tag{4}$$

and

$$H_0=\sum_{i=1}^{N}(T_i+V_i). \tag{5}$$

The states Φ_n are determinants composed of single-particle states φ_i, which are obtained from the equation

$$(T+V)\varphi_i=\epsilon_i\varphi_i. \tag{6}$$

It is also possible to consider unperturbed states Φ_n which are a linear combination of determinants.[6] The states φ_i occupied in Φ_n are called unexcited states. The remaining solutions of Eq. (6) are called excited states. An unoccupied unexcited state is called a hole and an occupied excited states is called a particle.

The BG result is

$$\psi_m=\sum_L\left(\frac{1}{E_m^{(0)}-H_0}H'\right)^n\Phi_m, \tag{7}$$

assuming that the energy denominators $(E_m^{(0)}-H_0)$ do not vanish. The $\sum_L$ means that only "linked" terms are to be included[2] and

$$H'=\sum_{i<j}^{N} v_{ij}-\sum_{i=1}^{N} V_i. \tag{8}$$

Also,

$$E_m-E_m^{(0)}=\langle\Phi_m|H'|\psi_m\rangle. \tag{9}$$

B. Multiple Perturbations

We now suppose that the atom is perturbed by a small external potential

$$\sum_{i=1}^{N} v_{ex}(r_i).$$

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[1] K. A. Brueckner, Phys. Rev. **97**, 1353 (1955); **100**, 36 (1955); *The Many-Body Problem* (John Wiley & Sons, Inc., New York, 1959).

[2] J. Goldstone, Proc. Roy. Soc. (London) **A239**, 267 (1957).

[3] H. P. Kelly, Phys. Rev. **131**, 684 (1963).

[4] H. P. Kelly and H. S. Taylor, J. Chem. Phys. **40**, 1478 (1964).

[5] H. P. Kelly, Phys. Rev. **136**, B896 (1964).

[6] H. P. Kelly, Phys. Rev. **144**, 39 (1966).

This treatment may also be used when there is more than one type of perturbing potential V_{ex} present. The BG perturbation theory may still be used to calculate the exact nonrelativistic energy and wave function in the presence of V_{ex} with the single-particle states φ_i used as a basis set for the expansion. We now have a double perturbation expansion starting from the unperturbed state Φ_n. The perturbation is

$$H'=\sum_{i<j}^{N} v_{ij}-\sum_{i=1}^{N} V_i+\sum_{i=1}^{N} V_{\mathrm{ex}}(r_i)\,, \tag{10}$$

and the usual BG linked-cluster expansion is carried out with this H'. The shift in energy due to V_{ex} is given by all energy diagrams in which an interaction with V_{ex} occurs at least once.

III. POLARIZABILITIES

A. Linked-Cluster Expansion

Among the more useful applications of multiple perturbation theory is the calculation of atomic polarizabilities and shielding factors. An extensive discussion of these quantities may be found in a review article by Dalgarno.[7] In such calculations we consider an atom perturbed by a small charge Z' located a distance r' from the nucleus of charge Z. We choose r' to be along the z axis. The interaction energy between the charge Z' and the atom is given in atomic units (a.u.) by

$$V_{\mathrm{int}}=\frac{ZZ'}{r'}-Z'\sum_{i=1}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}'|}\,, \tag{11}$$

$$V_{int}=\frac{ZZ'}{r'}-Z'\sum_{i=1}^{N}\sum_{k=0}^{\infty}\left(\frac{r_<^{\,k}}{r_>^{\,k+1}}\right)_i P_k(\cos\theta_i)\,, \tag{12}$$

where

$$(r_<^{\,k}/r_>^{\,k+1})_i=r_i^{\,k}/r'^{\,k+1} \tag{13}$$

for $r_i<r'$, and

$$(r_<^{\,k}/r_>^{\,k+1})_i=r'^{\,k}/r_i^{\,k+1} \tag{14}$$

for $r_i>r'$.

In calculating polarizabilities and shielding factors, we assume $r'>r_i$ for all i. However, in calculating polarization potentials we calculate a shift in energy due to Z' as a function of r' and the possibility $r_i>r'$ must also be considered. When $r_i<r'$ always,

$$V_{\mathrm{int}}(r_i<r')=\frac{Z'(Z-N)}{r'}-Z'\sum_{i=1}^{N}\sum_{k=1}^{\infty}\frac{r_i^{\,k}}{r'^{\,k+1}}P_k(\cos\theta_i)\,. \tag{15}$$

If $V_{\mathrm{int}}(r_i<r')$ is taken as V_{ex} in the multiple perturbation expansion, then

$$\psi_n=\psi_n^{(0)}+Z'\sum_{k=1}^{\infty}\psi_{n,1}^{(k)}/r'^{\,k+1}+O(Z'^2)\,, \tag{16}$$

where $\psi_n^{(0)}$ is the exact nonrelativistic wave function for the nth state in the absence of the perturbing Z' and $\psi_{n,1}^{(k)}$ is the function $\psi_n^{(0)}$ perturbed once by the interaction

$$V_{\mathrm{ex}}^{(k)}=-\sum_{i=1}^{N} r_i^{\,k}P_k(\cos\theta_i)\,. \tag{17}$$

Note that $\psi_n^{(0)}$ corresponds to ψ_n of Eq. (3). In the BG expansion $\psi_n^{(0)}$ is given by all diagrams starting from Φ_n with interactions with the perturbation H' of Eq. (8) but with no interactions with the external perturbation of Eq. (17). The term $\psi_{n,1}^{(k)}$ is given by all diagrams in which $V_{\mathrm{ex}}^{(k)}$ acts once and only once and for which Φ_n is the unperturbed state.

The 2^L-pole polarizability α_2L for the state $\psi_n^{(0)}$ may be defined by[7]

$$\alpha_2L=2\langle\psi_{n,1}^{(L)}|\sum_{i=1}^{N} r_i^{\,L}P_L(\cos\theta_i)|\psi_n^{(0)}\rangle/\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle\,. \tag{18}$$

The terms contributing to α_2L may be represented by diagrams.[5] Factorization of diagrams contributing to the numerator of Eq. (18) yields a factor $\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle$ which cancels the denominator. It is important to note that there are exclusion-principle-violating (EPV) diagrams resulting from this factorization.[5] The definition of α_2L in Eq. (18) is equivalent to defining[7]

$$\alpha_2L=-2E_{n,2}^{(L)}(t)\,, \tag{19}$$

where $E_{n,2}^{(L)}(t)$ is the sum of all linked-cluster energy diagrams with two interactions with $V_{\mathrm{ex}}^{(L)}$ for the unperturbed state Φ_n. The number of interactions with H' in Eq. (8) is unrestricted. The symbol $E_{n,2}^{(L)}$ will be used for the second-order contribution to $E_{n,2}^{(L)}(t)$.

In calculating shielding factors, $r_i^{\,L}$ in Eq. (18) is replaced by $r_i^{-(L+1)}$.

Second- and third-order diagrams contributing to $E_{n,2}^{(L)}(t)$ or to α_2L are shown in Fig. 1. The lowest order diagram, shown in Fig. 1(a), does not include any correlations among electron pairs. There is one correla-

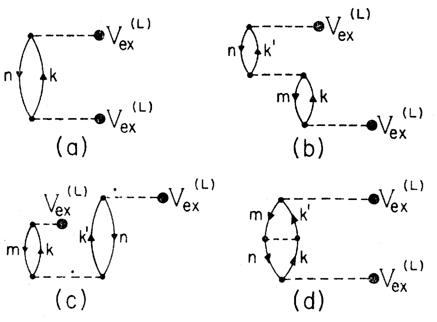

FIG. 1. Lowest order diagrams contributing to $E_{n,2}^{(L)}(t)$. (a) Second-order diagram. Diagrams (b), (c), and (d) are third-order and contain one correlation interaction. The diagram obtained by inverting (c) should also be included in addition to the exchange of (c). When the Hartree-Fock potential is used to calculate the single-particle states, it is possible to have $m=n$ in diagram (d).

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

tion interaction in each third-order diagram shown in Figs. 1(b), 1(c), and 1(d). Note that these third order diagrams are second order in $V_{\mathrm{ex}}{}^{(L)}$ and first order in the correlation interaction H'. It is possible to include the effects of repeated correlation interactions in diagrams like that of Fig. 1(c) by the methods of summing diagrams used for correlation energies.[5] These diagrams were previously evaluated in a calculation of the dipole and quadrupole polarizabilities and shielding factors of the beryllium atom.[5] The diagrams of Fig. 1(d) with $m=n$ enter only when the Hartree-Fock potential is used to calculate all single particle states and these terms are then large. When the states φ_i are determined as for the present work, these diagrams with $m=n$ do not occur or in effect have been summed. The beryllium calculation also included effects from diagrams with two or more correlation interactions. Typical diagrams are shown in Fig. 2. Diagrams (f), (g), and (h) of Fig. 2 are rearrangement diagrams[8] and contain EPV effects when two or more hole lines refer to the same state.

B. The Open-Shell Case

In the case of atomic states with unfilled shells, there is an energy degeneracy in M_L and M_S. However, the BG theory may still be applied provided the perturbation does not lead to excited states which cause the energy denominators in the perturbation expansion to vanish.[6] The correlation-energy results are independent of M_L and M_S.[6] However, polarizabilities and shielding factors depend on M_L and should be averaged over M_L. They are independent of M_S, since in these cases

$$[S,V_{\mathrm{ex}}]=0. \tag{20}$$

Unperturbed wave functions for the $(2p)^4$ configuration for atomic oxygen are given in Table I. The notation $+1^+$ refers to a $2p$ electron with $m_l=+1$ and $m_s=+\frac{1}{2}$; 0^+ refers to a $2p$ electron with $m_l=0$ and $m_s=+\frac{1}{2}$, etc. In calculating the dipole polarizability α_d for the ^3P and ^1D states of oxygen, the average over M_L was carried out as required. In calculations for the ^3P state, an average over M_S was also made and it was found explicitly that α_d is independent of M_S as required by Eq. (20).

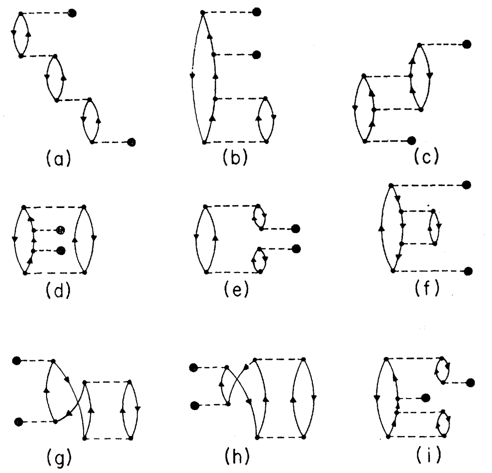

FIG. 2. Typical fourth-order diagrams contributing to $E_{n,2}{}^{(L)}$ or to $\alpha_2{}^L$. The heavy dot represents an interaction with $V_{\mathrm{ex}}{}^{(L)}$ given by Eq. (17). Higher order terms may be obtained by including the effects of further correlations among electron pairs in these diagrams. In diagram (b) the lower dot interaction may also come between the two correlation interactions. In diagram (d) either or both dot interactions may be associated also with the particle line on the right. Diagrams (f), (g), and (h) are called rearrangement diagrams. Diagram (i) is a typical fifth-order term.

C. Single-Particle States

The single-particle states φ_i used in the present calculations are the same φ_i calculated previously for the determination of correlation energies in oxygen.[6] The $l=1$ wave functions were calculated in the field of neutral oxygen minus one $2p$ electron. The exchange coefficients with $1s$, $2s$, and $2p$ states were such that the lowest $l=1$ solution is the Hartree-Fock (HF) $2p$ solution for the ^3P ground state. The $l=2$ states were also calculated in the field of neutral oxygen minus one $2p$ electron. The $l=0$ states were calculated in the field of neutral oxygen minus one $2s$ electron. The remaining $2s$ state is the restricted HF $2s$ solution for the ^3P state. Further details may be found in Ref. 6.

TABLE I. Unperturbed $(2p)^4$ wave functions for oxygen.[a]

State	Unperturbed wave function
^3P ($M_L=+1; M_S=+1$)	$(+1^+0^+-1^++1^-)$
^3P ($M_L=0; M_S=+1$)	$(+1^+0^+-1^+0^-)$
^3P ($M_L=-1; M_S=+1$)	$(+1^+0^+-1^+-1^-)$
^1D ($M_L=+2$)	$(1^+0^+0^-+1^-)$
^1D ($M_L=+1$)	$(1/\sqrt{2})[(+1^+-1^+0^-+1^-)$ $+(+1^+0^+-1^-+1^-)]$
^1D ($M_L=0$)	$(1/\sqrt{6})[(0^+-1^+0^-+1^-)$ $+2(+1^+-1^+-1^-+1^-)$ $+(+1^+0^+-1^-0^-)]$
^1D ($M_L=-1$)	$(1/\sqrt{2})[(0^+-1^+-1^-+1^-)$ $+(+1^+-1^+-1^-0^-)]$
^1D ($M_L=-2$)	$(0^+-1^+-1^-0^-)$
^1S	$(1/\sqrt{3})[(0^+-1^++1^-0^-)$ $+(+1^+0^+0^--1^-)$ $-(+1^+-1^++1^--1^-)]$

[a] The wave functions show the assignment of m_l and m_s values to the $2p$ electrons. For example, $+1^+$ refers to a $2p$ state with $m_l=+1$ and $m_s=+\frac{1}{2}$; 0^+ refers to $m_l=0$ and $m_s=+\frac{1}{2}$.

If was pointed out in Ref. 5 that it is desirable to have the excited φ_i's correspond approximately to physical single-particle excitations of the atom. When the ground-state HF potential is used to calculate all φ_i's, then the excited states are calculated in the field of the nucleus and N electrons rather than in the field of the nucleus and $N-1$ electrons, which is the case for

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[8] K. A. Brueckner and D. T. Goldman, Phys. Rev. 117, 207 (1960).

true excitations.[3] In the case of neutral oxygen and beryllium all excited φ_i's (in the BG sense) are in the continuum if calculated with the HF potential.[3,6] As a result of using the HF potential, the perturbation expansion may converge slowly.[3] In calculating polarizabilities and shielding factors there are important contributions from diagrams of the type shown in Fig. 1(d) with hole lines m and n referring to the same state when the HF potential is used.[5] In the present calculation with excited states φ_i corresponding to physical single particle excitations of the atom, the diagrams of Fig. 1(d) with $m=n$ do not contribute.

Since the present calculations used a fixed set of single-particle states to calculate polarizabilities for various excited states of the atom, there are contributions from diagrams with interactions with passive unexcited states[2] as shown in Fig. 3. Diagrams (a), (b), and (c) of Fig. 3, and their corresponding higher iterations, were summed as in Ref. 6 to give the second-order term shown in Fig. 1(a), with the original single-particle energies replaced by the more accurate appropriate energies for the hole line and the particle line. Contributions from diagrams of the types (d) and (e) of Fig. 3 were not included but are expected to be relatively small compared to the second-order term for the states considered, since the net effect of interactions with the passive unexcited states and with the potential V is small for the outer electron in these cases.

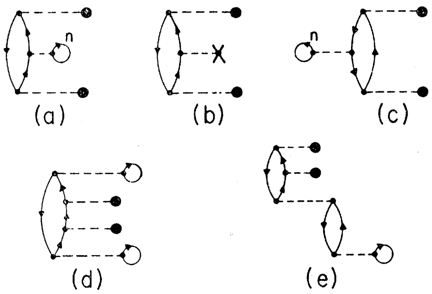

FIG. 3. Interactions with passive unexcited states. The heavy dot represents an interaction with $V_{\text{ex}}^{(L)}$. The cross in (b) represents an interaction with the potential V which is used to calculate the single-particle states. Diagrams (a), (b), and (c) and higher iterations may be summed to obtain corrections to the single-particle energies ϵ_i used in calculating the second-order diagram of Fig. 1(a).

D. Numerical Results for the Ground State

The contributions from the diagrams of Fig. 1(a) are given by

$$E_{n,2}^{(1)}=\sum_{m,k}\frac{|\langle k|r\cos\theta|m\rangle|^2}{\epsilon_m-\epsilon_k}. \tag{21}$$

The sum over m includes all single-particle states occupied in Φ_n. The sum over k includes all excited states. For the ^3P ground state of oxygen, radial contributions to $-E_{n,2}^{(1)}$ (in a.u.) from excitations of a single $2p$ electron into $l=2$ states are given in Table II. The values given do not include the angular factors which are 3/15 for a $2p$ electron with $m_l=\pm1$ and 4/15 for $m_l=0$. Note that the perturbation $r\cos\theta$ commutes with l_z and so conserves m_l in the excitation. The most important $2p$ excitations are into continuum states. The radial contributions to $-E_{n,2}^{(1)}$ from excitations of a $2p$ electron into $l=0$ states are given in Table III. The angular factor of $\frac{1}{3}$ is not included. Table IV contains the radial contributions to $-E_{n,2}^{(1)}$ from excitations of a single $2s$ electron; the angular factor is $\frac{1}{3}$. The sums over the infinite number of bound excited states may be carried out by the n^{-3} rule.[5] Sums over the continuum are evaluated by numerical integration.[3,5]

In calculating the polarizability α_d for the ^3P state, we average over M_L. It is necessary then to calculate α_d for $M_L=\pm1$, 0. The calculation is carried out for $M_S=+1$, but the results are independent of M_S because of Eq. (20). This was also checked by carrying out the sum over M_S explicitly. From Table I it is observed that for $M_L=+1$ there are three $2p$ electrons with $m_l=\pm1$ and one with $m_l=0$. The angular factor

TABLE II. Radial contributions to $-E_{n,2}^{(1)}$ for ^3P oxygen from $2p\rightarrow md$ excitations.[a]

m	$E_{n,2}^{(1)}$ *in* a.u.
3	0.08555
4	0.04175
5	0.02229
6	0.01313
7	0.00834
8	0.00562
9	0.00396
$\sum_{m=10}^{\infty}$	0.01583
Continuum	1.65209
Total	1.84856

[a] Values given are for a single $2p$ electron. The contribution to $-E_{n,2}^{(1)}$ from a single electron is the product of the radial contribution and the angular factor, which is 3/15 for $2p$ ($m_l=\pm1$) and 4/15 for $2p$ ($m_l=0$).

TABLE III. Radial contirbutions to $-E_{n,2}^{(1)}$ for ^3P oxygen from $2p\rightarrow ms$ excitations.[a]

m	$-E_{n,2}^{(1)}$ in a.u.
3	0.6194
4	0.0792
5	0.0260
6	0.0119
7	0.0065
8	0.0039
$\sum_{n=9}^{\infty}$	0.0122
Continuum	0.2548
Total	1.0138

[a] Values given are for a single $2p$ electron. The contribution to $-E_{n,2}^{(1)}$ from a single electron is given by the above radial contribution times the angular factor which is $\frac{1}{3}$.

TABLE IV. Radial contributions to $-E_n\langle_2^{(1)}$ for ^3P oxygen from $2s \rightarrow mp$ excitations.[a]

m	$-E_{n,2}^{(1)}$ in a.u.
2	2.1403[b]
3	0.0068
4	0.0023
5	0.0010
6	0.006
7	0.003
8	0.0002
$\sum_{m=9}^{\infty}$	0.007
Continuum	0.0942
Total	2.2464

[a] Values are for a single $2s$ electron. The contribution to $-E_{n,2}^{(1)}$ is given by the values in the table times the angular factor $\frac{1}{3}$.
[b] This value also includes sums of higher order terms as shown in Figs. 3(a), 3(b), and 3(c). Summing these terms modifies the single-particle energies used in calculating the diagram of Fig. 1(a).

is 3/15 for $m_l = \pm 1$ and 4/15 for $m_l = 0$, and for all four electrons it is 13/15.[9] The total second-order contribution to α_d in this case from $2p \rightarrow nd$ excitations is obtained by multiplying the value 1.8486 from Table I by the angular factor 13/15 and by 2 since in second order

$$\alpha_2 L = -2E_{n,2}^{(L)}.$$

The result is α_d equals 3.2042 atomic units (a.u.). However, it is customary to give α_d in Å^3 (10^{-23} cm^4). Then α_d in a.u. is multiplied by 0.14818 to convert to Å^3. For $M_L = +1$, the contribution to α_d from $2p \rightarrow nd$ excitations is 0.4748 Å^3. There is also a contribution to α_d from $2p$ $(m_l = 0) \rightarrow ns$ as shown in Table III equal to 0.10015 Å^3. Contributions to α_d from $2s$ electrons are given in Table IV. The $2s^-$ electron may be excited into all np^- $(m_l = 0)$ states including the unoccupied $2p^-$ $(m_l = 0)$ state. The $2s^+$ electron, however, cannot be excited into the $2p$ (0^+) state which is already occupied. For $2s$ electrons the angular factor is $\frac{1}{3}$ and the total contribution to α_d $(M_L = +1)$ is 0.2324 Å^3. There is also a small contribution of 0.00034 Å^3 from the two $1s$ electrons. The sum of all these contributions to α_d for the $M_L = +1$ state is 0.8077 Å^3.

TABLE V. Total second-order contributions to the dipole polarizability in Å^3 for oxygen ^3P.[a]

Excitations[b]	$M_L = \pm 1$	$M_L = 0$
$2p \rightarrow nd$	0.47479	0.51131
$2p \rightarrow ns$	0.10015	0.20030
$2s \rightarrow np$[c]	0.23250	0.02097
$1s \rightarrow np$	0.00034	0.00028
Total	0.80768 Å	0.73286 Å^3

[a] 1 Å $= 10^{-8}$ cm.
[b] Excitations into the continuum are included.
[c] Higher order diagrams of Figs. 3(a), 3(b), and 3(c) are included.

For the ^3P $(M_L = 0)$ state the contribution to α_d from $2p \rightarrow nd$ excitations is 0.5113 Å^3 because the total angular factor is now 14/15. There are now two $2p$ $(m_l = 0)$ electrons which may be excited into ns states resulting in a total $2p \rightarrow ns$ contribution of 0.2003 Å^3. The $2s \rightarrow np$ result is only 0.02097 Å^3 since both $2p$ $(m_l = 0)$ states are occupied. The $1s \rightarrow np$ result is 0.00028 Å^3. The sum of these contributions to α_d $(M_L = 0)$ is 0.73286 Å^3. A summary of the various contributions for $M_L = +1$ and $M_L = 0$ is given in Table V. The value for α_d $(M_L = -1)$ is the same as for α_d $(M_L = +1)$ and the average over M_L is 0.78274 Å^3.

Third-order contributions to α_d include correlations as shown in Fig. 1(b), 1(c), and 1(d). The total calculated result for diagrams (b) and (c), when either state m or n is $2s^-$ and the other hole is a $2p^+$ state, is -0.153 Å^3 for $M_L = \pm 1$. For $M_L = 0$, the result is very small since $2s$ excitations into $2p$ states through $V_{\text{ex}}^{(1)}$ cannot occur because of the exclusion principle. Correlations among the $2s^-$ and $2p^-$ states have been omitted since diagrams (b) and (c) are expected to be essentially cancelled by exchange diagrams such as shown in Fig. 1(d). The average of these third-order terms over M_L is -0.1018 Å^3. Diagrams (b) and (c) have also been calculated when both hole states are $2p$. The total result is -0.0394 Å^3 for $M_L = \pm 1$ and -0.0525 Å^3 for $M_L = 0$; the average over M_L is -0.0438 Å^3. Third-order diagrams then reduce the second order result by approximately -0.1456 Å^3. Fourth-order diagrams shown in Fig. 2 should also be considered and the largest effects come from diagrams (a) through (e), which increase α_d. Estimates of the magnitudes of the fourth-order diagrams indicate that they approximately cancel the reduction in α_d due to the third-order terms. The value 0.7827 Å^3 calculated in second order is then taken as the value for α_d in this case.

E. Numerical Results for Excited States

Calculations of α_d for the $(2p)^4$ ^1D and $(2p)^4$ ^1S states of oxygen have also been carried out. Single-particle energies used in these second-order calculations were modified to include effects of diagrams of Fig. 3(a), 3(b), and 3(c). The $2s$ and $2p$ energies were obtained from the Hartree-Fock calculations of Clementi, Roothaan, and Yoshimine.[10] The assignment of m_l and m_s values to $2p$ electrons is given in Table I. The result is 0.7633 Å^3 for ^1D $(M_L = \pm 2)$, 0.7946 Å^3 for ^1D $(M_L = \pm 1)$, and 0.8330 Å^3 for ^1D $(M_L = 0)$. The average over M_L is 0.7898 Å^3 for the ^1D state in second order. For the ^1S state, the second-order value for α_d is 0.8357 Å^3.

The dipole polarizability has also been calculated for a number of additional excited states in which one electron is in an excited $3s$, $3p$, or $4s$ state outside of a $(2p)^3$ ^4S core. In such cases α_d is determined almost

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[9] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1957), p. 178.

[10] E. Clementi, C. C. J. Roothaan, and M. Yoshimine, Phys. Rev. **127**, 1618 (1962).

TABLE VI. Contributions to α_d for oxygen $(2p)^3\,{}^4S\;3s\;{}^5S$.

Excitation	Contribution to α_d (Å^3)
$3s\rightarrow 3p$	47.06896
$4p$	0.06700
$5p$	0.00349
$6p$	0.00046
$7p$	0.00009
$8p$	0.00003
$\sum_{9p}^{\infty}$	0.00004
Continuum	0.02690
Total	47.16696 Å^3

completely by the contributions from the outer electron. The lowest of these states is the $(2p)^3\,{}^4S\;3s\;{}^5S$ state and the contributions to α_d for this case are given in Table VI. The largest contribution comes from the "resonance" transition $3s\rightarrow 3p$, unlike the ground-state case where the greatest contribution of $2p$ excitations into d states comes from the continuum. A summary of all calculated polarizabilities is given in Table VII. The $(2p)^3\,{}^4S\;3s\;{}^3S$ results differ from the $3s{}^5S$ results because of the single particle energies being modified to include the diagrams of Fig. 3(a), (b), and (c). For the $4s{}^5S$ state, the $4s\rightarrow 4p$ transition contributes 847.95 Å^3 and the $4s\rightarrow 3p$ transition contributes -49.43 Å^3. The remaining excitations, although included, are small.

Most of the result for the $3p{}^5P$ state comes from $3p\rightarrow nd$ excitations which contribute 64.30 Å^3; the $3p\rightarrow 3d$ excitation contributes 61.60 Å^3. There is also 5.204 Å^3 from $3p\rightarrow ns$ excitations. The $3p\rightarrow 4s$ value of 49.43 Å^3 is almost cancelled by -47.07 Å^3 from the $3p\rightarrow 3s$ transition.

In calculations for more highly excited states than those listed, the cancellation between different contributions becomes large and it is necessary to determine the separate excitations to great accuracy. For example, the large $4p\rightarrow 4d$ contribution to α_d is nearly cancelled by the $4p\rightarrow 3d$ negative result.

IV. POLARIZATION POTENTIALS

A charge Z' at a distance r' from the nucleus has an interaction with the atom given by Eq. (11) or (12) if the Legendre expansion is used. This energy may be calculated by multiple perturbation theory and in first order it is, for the unperturbed state Φ_n,

$$E_{n,1}=\langle\Phi_n|\,V_{\rm int}\,|\Phi_n\rangle. \tag{22}$$

TABLE VII. Calculated polarizabilities α_d for oxygen.

State	α_d in Å^3
$(2p)^4\,{}^3P$	0.7827
$(2p)^4\,{}^1D$	0.7898
$(2p)^4\,{}^1S$	0.8357
$(2p)^3\,{}^4S\,3s\,{}^5S$	47.17[a]
$(2p)^3\,{}^4S\,3s\,{}^3S$	50.63[a]
$(2p)^3\,{}^4S\,4s\,{}^5S$	800.97[a]
$(2p)^3\,{}^4S\,4s\,{}^3S$	831.73[a]
$(2p)^3\,{}^4S\,3p\,{}^5P$	69.50[a]

[a] Contributions from the outermost electron only.

There are second order and higher perturbations due to the terms

$$-Z'\sum_{i=1}^{N}\sum_{k=0}^{\infty}\left(\frac{r_<^{\,k}}{r_>^{\,k+1}}\right)_i P_k(\cos\theta_i). \tag{23}$$

We may use the BG expansion to calculate the resulting shift in energy for the state Φ_n in the same way that $E_{n,2}{}^{(1)}(t)$ and α_d were calculated in the previous section. However, we do not restrict r' to be greater than all r_i as we do for the α_d calculation, and so the $k=0$ term $-Z'/r_>$ contributes, in general, to the energy shift. The second order terms are shown in Fig. 1(a), with the external potential being $Z'V_p{}^{(k)}$ where

$$V_p{}^{(k)}=-\sum_{i=1}^{N}\left(\frac{r_<^{\,k}}{r_>^{\,k+1}}\right)_i P_k(\cos\theta_i). \tag{24}$$

The second order terms of Fig. 1(a) should be calculated for each $V_p{}^{(k)}$ starting with $k=0$. The resulting shift in energy for the state Φ_n is dependent on the distance r′. The second-order energy terms for the external potential $Z'\sum_{k=0}^{\infty}V_p{}^{(k)}$ are proportional to Z'^2. Higher order terms in the correlation interaction but second order in $Z'V_p{}^{(k)}$ are shown in Figs. 1, 2, and 3. This second order shift in energy as a function of r' gives a polarization potential $V_{\rm polz}(r')$. It is an approximation to the second order term of the optical potential $\mathcal{V}_{c2}(r')$ as discussed, for example, by Goldberger and Watson[11] and by Mittleman and Watson.[12]

As $r'\rightarrow\infty$

$$\mathcal{V}_{c2}(r')\cong-\alpha_d Z'^2/2r'^4, \tag{25}$$

with α_d in atomic units.[11] As pointed out by Goldberger and Watson, it has been customary to use a "cutoff" to avoid the singularity as $r'\rightarrow 0$.

$$\mathcal{V}_{c2}(r')\rightarrow\mathcal{V}_p(r')\equiv-\alpha_d Z'^2/2(r'^2+S^2)^2, \tag{26}$$

where S is a length related to the atomic size, and Mittleman and Watson[12] estimate

$$S^4\cong\tfrac{1}{2}\alpha_d Z^{-1/3}. \tag{27}$$

When $V_{\rm polz}(r')$ is used to approximate $\mathcal{V}_{c2}(r')$, there is no need to insert a cutoff since $V_{\rm polz}(r')$ remains finite as r′ → 0. This is because in Eq. (24) we use $r_<$ and $r_>$ rather than $r'>r_i$. An important application of polarization potentials is in scattering calculations as discussed by LaBahn and Callaway[13] and by Stone.[14]

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[11] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1964), p. 853.

[12] M. H. Mittleman and K. M. Watson, Phys. Rev. **113**, 198 (1959).

[13] R. W. LaBahn and J. Callaway, Phys. Rev. **135**, A1539 (1964).

[14] P. M. Stone, Phys. Rev. **141**, 137 (1966).

TABLE VIII. Polarization potential $-V_{\text{polz}}(r)$ for oxygen $(2p)^3\,{}^4S\,3d\,{}^5S$ in a.u.

r	Monopole contribution	Dipole contribution	Total $-V_{\text{polz}}(r)$	$\alpha_d/2r^4$
0.00	0.1196	0.0000	0.1196	∞
0.10	0.1069	0.0005	0.1074	1.592×10^6
0.20	0.954	0.0023	0.0977	9.947×10^4
0.40	0.0871	0.0109	0.0980	6217.0
0.60	0.0811	0.0187	0.0998	1228.1
0.80	0.0726	0.0228	0.0955	388.6
1.00	0.0644	0.0255	0.0899	159.2
1.40	0.0533	0.0330	0.0863	41.43
2.00	0.0450	0.0544	0.0994	9.947
2.40	0.0404	0.0719	0.1123	4.797
3.00	0.0317	0.0939	0.1256	1.965
3.40	0.0254	0.1023	0.1277	1.1910
3.80	0.0193	0.1052	0.1245	0.7633
4.20	0.0142	0.1032	0.1175	0.5115
4.60	0.0101	0.0978	0.1079	0.3555
5.00	0.0070	0.0901	0.0971	0.2546
5.96	0.0027	0.0684	0.0711	0.1261
7.00	0.0009	0,0473	0.0482	0.0663
9.00	0.0001	0.0220	0.0221	0.0243
11.00	0.0000	0.0106	0.0106	0.0109
15.00	0.0000	0.0031	0.0031	0.0031

The polarization potentials may be particularly important in the scattering of electrons from excited states of atoms since in such cases the polarizabilities are large.

In this work the polarization potential for $Z'=1$ has been calculated for the $(2p)^3\,{}^4S\,3s\,{}^5S$ excited state of oxygen. Only $k=0$ (monopole) and $k=1$ (dipole) interactions of Eq. (24) have been included. These were calculated to second order for the $3s$ electron. Contributions from the $(1s)^2\,(2s)^2\,(2p)^3$ core have been omitted. Since these core electrons contribute little to α_d for the $3s{}^5S$ state, it is expected that their contributions to $V_{\text{polz}}(r')$ are small except for small values of r' where $V_{\text{polz}}(r')$ is relatively small compared to the Hartree-Fock potential. However, a more accurate calculation of $V_{\text{polz}}(r')$ would include effects from all electrons and from all values of k in Eq. (24).

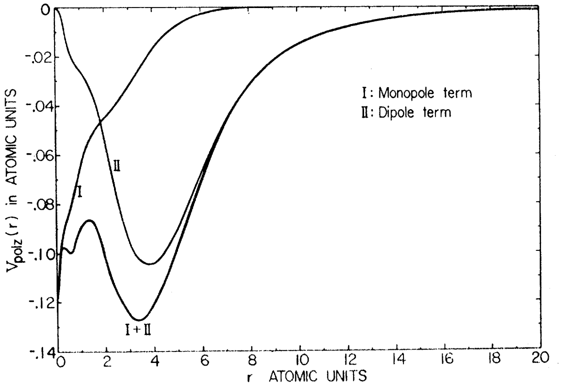

FIG. 4. The polarization potential$+V_{\text{polz}}(r)$ from excitations of the $3s$ electron in the $(2p)^3\,{}^4S\,3s\,{}^5S$ state of oxygen. The monopole ($k=0$) and dipole ($k=1$) contributions from the interaction of Eq. (23) are shown separately.

Results of the calculations of $V_{\text{polz}}(r)$ are listed in Table VIII along with the approximate potential $\alpha_d/2r^4$. The comparison is improved when $\mathcal{V}_p(r)$ of Eq. (26) is used. For example, $\mathcal{V}_p(r)$ is -0.4956 at $r=3.00$. The monopole and dipole contributions to $V_{\text{polz}}(r)$ from the $3s$ electron and their sum are plotted in Fig. 4.

For large r most of the monopole and dipole terms come from the $3s\rightarrow3p$ excitations. For small r, other excitations, especially to the continuum, become important. Continuum excitations give approximately one-half of the monopole term and 15% of the dipole term as $r\rightarrow0$.

V. DISCUSSION AND CONCLUSIONS

In Sec. III, α_d for the oxygen ground state was calculated to be 0.783 Å^3 in second order. The third-order result reduces this value by approximately 0.146 Å^3. However, the estimated contribution of the fourth-order terms is approximately equal and opposite to the third-order result. The estimates may be made from a knowledge of the sizes of matrix elements already calculated for lower orders and from the sizes of the oxygen correlation energy diagrams.[6] Although the numerical work is fairly lengthy, these terms could be calculated exactly as shown previously.[5]

The present second-order result of 0.783 Å^3 may be compared with the experimental value 0.77±0.06 Å^3 obtained by Alpher and White.[15] A calculated value of 0.89 Å^3 was obtained by Dalgarmo and Parkinson using the Sternheimer method[16]; and a value of 0.829 Å^3 was obtained by Klein and Brueckner using a semi-empirical approach.[17] Although the second-order result is this case is in good agreement with experiment, it was not so in the previous beryllium calculation[5] of α_d where third-order terms reduced the second order result of 12.15 Å^3 by a factor of 0.470 to a value 5.57 Å^3 The calculated fourth-order terms only partially compensated for this reduction bringing the total to 6.93 Å^3. Explicit calculation of third-order terms in the oxygen ${}^3P$ case shows that the second-order result is reduced only by a factor of 0.813. The increased relative size of the fourth-order oxygen result so that it approximately cancels the third-order terms is partially due to the fact that both $l=1$ and $l=2$ excitations are important in calculating correlations among $2p$ electrons in oxygen.[6] For Be the correlations among the outer $2s$ electrons come mostly from $l=1$ excitations.[3] The diagrams of Fig. 2(d) with each particle line having one interaction with $V_{\text{ex}}{}^{(1)}$ are more important for oxygen since the matrix elements $\langle 2p2p|v|kdk'd\rangle$ and $\langle kpk'p|v\times|2p2p\rangle$ are now both significant.

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[15] R. A. Alpher and D. R. White, Phys. Fluids **2**, 153 (1959).

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

[17] M. M. Klein and K. A. Brueckner, Phys. Rev. **111**, 1115 (1958).

The polarizability α_d of the oxygen ^1D state was calculated in second order to be 0.790 Å^3 and α_d for ^1S was found to be 0.836 Å^3. The correlation contributions from third- and fourth-order terms in these cases were omitted. There is a possible source of error in the ^1D and ^1S calculations because of the use of $2s$ and $2p$ orbitals appropriate to the ^3P state. However, the differences between single particle orbitals for these three states are relatively small.[10] Effects due to differences in single-particle energies for these states have been included.

Polarizabilities were also calculated in second order for excited states of oxygen in which one of the original $2p$ electrons is in an excited $3s$, $4s$, or $3p$ state outside of a $(2p)^3\ {}^4S$ core. In these cases α_d is much greater than for the $(2p)^4$ configuration. Only contributions to α_d from the outer electron were considered and the contributions from the core electrons are estimated as less than one percent of α_d. Third- and fourth-order terms are expected to be small relative to the second-order term since the outer electron is at a large distance from the core electron and so correlation effects should be small.

In the calculations of this paper, perturbation terms are evaluated by explicit sums over intermediate states. An alternative approach is to solve the equivalent perturbation equations.[7] Sternheimer[18] and others[7] have solved numerically the first-order equation

$$(H_0-E_0)\Phi_{n,1}{}^{(k)}=-V_{\mathrm{ex}}{}^{(k)}\Phi_n \tag{28}$$

for a number of atoms. The solutions are, of course, dependent on the choice of H_0. Then for
$\langle\Phi_n|\Phi_{n\,1}{}^{(k)}\rangle=0$,

$$\alpha_2L=2\langle\Phi_n|\sum_{i=1}^{N} r_i{}^LP_L(\cos\theta_i)|\Phi_{n,1}{}^{(L)}\rangle \tag{29}$$

in the lowest order approximation. Equations (28) and (29) are equivalent to Eq. (21) (to within the factor -2) provided H_0 of Eq. (28) is used to calculate the single particle states used in Eq. (21). When H_0 is the Hartree-Fock Hamiltonian,[7] use of Eqs. (28) and (29) is referred to as the uncoupled Hartree-Fock method.[7] It was pointed out by Kelly and Taylor[4] that second-order calculations of α_2L by the pertubation technique of Eq. (21) when H_0 is the Hartree-Fock Hamiltonian are equivalent to the uncoupled Hartree-Fock method.

Use of Eqs. (28) and (29), however, does not include correlations. It has been shown[5] that the uncoupled HF method may give poor results because of important contributions to α_2L from terms shown in Fig. 1(d) with $m=n$. When single-particle states are chosen as in the work of this paper, diagram 1(d) with $m=n$ does not occur as discussed previously.[5] An improvement over the second-order values may be made by explicit calculation of the higher order diagrams shown in Figs. 1 and 2 or by use of the coupled Hartree-Fock method[19] or the variational methods discussed by Dalgarno.[7] The coupled Hartree-Fock method is equivalent to calculating all the diagrams of Fig. 1 and all higher iterations of these basic diagrams. For example, the diagram of Fig. 2(a) is included in the coupled HF method, but the remaining diagrams of Fig. 2 are not included. Applications of the variational method have been limited to atoms with few electrons.[7] The coupled HF method has been successfully applied to closed-shell atoms with up to ten electrons.[20–22] A more detailed comparison of these methods is included in a forthcoming review article.[23]

In Sec. IV it was shown how BG perturbation theory may be used in calculating V_{polz}, the polarization potential. The Hartree-Fock potential plus V_{polz} for a given state may be used to give an appropriate optical potential which may then be used in scattering calculations. Numerical results were obtained for V_{polz} for the $(2p)^3\ {}^4S\ 3s\ {}^5S$ excited state of oxygen. Only the monopole and dipole contributions from the $3s$ electron were included and correlation effects were omitted. However, it is possible with the BG theory to calculate contributions for all electrons and to include correlations and higher multipole terms.

One of the advantages of the Brueckner-Goldstone perturbation approach is its flexibility in coping with many different physical problems. For example, the single-particle wave functions used in a previous correction energy calculation were used in this work to calculate polarizabilities and a polarization potential. Also, information about electron correlation energy diagrams was used in estimating fourth order terms for the polarizability. Future applications of these methods will include a calculation of the polarization potential for the oxygen ground state.

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[23] H. P. Kelly (to be published).