

***Ab initio* calculation of frequency-dependent atomic dipole polarizability**

H. P. Saha

Department of Physics, University of Central Florida, Orlando, Florida 32816

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The polarized orbitals produced by simultaneous optimization of both bound and continuum multiconfiguration Hartree-Fock wave functions at each kinetic energy of the scattering electron in low-energy electron-atom collisions are used to calculate the frequency-dependent dipole polarizability of the ground state of atomic oxygen. Excellent agreement is obtained with experiment and other theoretical calculations, indicating that this *ab initio* approach is a powerful tool for determining accurate frequency-dependent atomic dipole polarizabilities.

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I. INTRODUCTION

When an electric field is applied to an atomic system the charge cloud of the atomic system is distorted and the system is polarized. The polarization is proportional to the electric field strength. If the field is oscillatory with frequency ω , as for example, in a radiation field, the polarizability is frequency dependent. It gives a measure of the dispersion of the incident radiation field due to processes which involve the absorption and subsequent emission of a single photon by the atom. The index of refraction and the Verdet constant can be calculated from a knowledge of the frequency-dependent polarizability. The van der Waals coefficients of the long-range interaction between two atoms can also be calculated from these dynamic dipole polarizabilities.

The present paper deals with the frequency-dependent polarizability of atomic oxygen. Kelly [1] used many-body perturbation theory with time-dependent perturbations to calculate the frequency-dependent polarizabilities of atomic oxygen. His results are in very good agreement with experiment. Allison, Burke, and Robb [2] calculated the frequency-dependent polarizability of atomic oxygen using the *R*-matrix method. They also determined van der Waals coefficients for atomic species by expressing them in terms of integrals over the atomic polarizabilities for imaginary frequency. Dalgarno and Parkinson [3] calculated the dipole polarizability of atomic oxygen using a theory based upon an antisymmetrized Hartree approximation. Their result was in satisfactory agreement with experiment. Henry [4] also determined the static dipole polarizability of atomic oxygen. He extended the method developed by Temkin [5] to include all direct contributions from the polarized orbitals and the exchange contribution from the most important type of

polarized orbital. His result agreed very well with experiment. On the experimental side, Alpher and White [6] made an accurate experimental measurement for the dipole polarizability and specific refractivity of atomic oxygen at several wavelengths. Very recently we applied the multiconfiguration Hartree-Fock (MCHF) method [7] to calculate static dipole polarizabilities for the closed shell atoms, helium, neon, and argon [8]. In these calculations polarized orbitals were calculated by optimizing the bound and continuum orbitals obtained for electron scattering at zero kinetic energy. The results agree extremely well with experimental measurement.

In the present paper we extended the MCHF method [7] to calculate the frequency-dependent polarizabilities of atomic oxygen by generating the frequency-dependent polarized orbitals to see how the polarizability changes with the change of frequency of the applied field. The aim of the present paper is to determine the polarized orbitals for each frequency of the applied field and then use them to calculate the frequency-dependent polarizability of the oxygen atom. The MCHF method has the capability of generating frequency-dependent polarized orbitals by optimizing both bound and continuum wave functions for each kinetic energy of the scattering electron. The main emphasis in this investigation is to take into account the electron correlation and the dynamical polarization effects *ab initio* in order to obtain accurate frequency-dependent polarized orbitals.

II. THEORY**A. Frequency-dependent dipole polarizabilities**

Following Allison, Burke, and Robb [2], the dynamic dipole polarizability of an atomic system in atomic units is defined as

$$\alpha_{M_L M_L' \mu \nu}(\omega) = 2 \sum_{k, L_s} \frac{(E_k - E_0) \langle \Phi_0(L M_L) | M_1^\mu | \Phi_k(L_s M_{L_s}) \rangle \langle \Phi_k(L_s M_{L_s}) | M_1^\nu | \Phi_0(L M_L') \rangle}{(E_k - E_0)^2 - \omega^2}.$$

The summations are taken over all states Φ_k , which are coupled to the initial ground state Φ_0 by the dipole operators

$$M_1^{\mu,\nu} = \sum_i \left[\frac{4\pi}{3} \right]^{1/2} r_i Y_1^{\mu,\nu}(\hat{\mathbf{r}}_i).$$

The explicit magnetic quantum number dependence of the polarizability can be separated out using the Wigner-Eckhart theorem, and $\alpha(\omega)$ can be written as

$$\alpha_{M_L M_L' \mu \nu}(\omega) = \sum_{L_s} C_{L_s 1}(L M_L'; M_L' - \mu \mu) \\ \times C_{L 1}(L_s M_L + \nu; M_L \nu) \bar{\alpha}^{L_s}(\omega),$$

where

$$\bar{\alpha}^{L_s}(\omega) = \frac{2}{3} \sum_k \frac{(E_k - E_0) \langle L \| M_1 \| n L_s \rangle \langle n L_s \| M_1 \| L \rangle}{(E_k - E_0)^2 - \omega^2}$$

and C 's are the Clebsch-Gordan coefficients. nl are the polarized orbitals. Evaluating the dipole matrix element $\langle L \| M_1 \| n L_s \rangle$ and pole positions $(E_k - E_0)$, the summation can be computed.

The polarized states Φ_k are solutions to the atomic Hamiltonian in the presence of the external field. The present approach is to determine these polarized wave functions through the MCHF procedure by selecting those bound states which are the solutions to the full Hamiltonian, with the scattering electron, for each kinetic energy, which in turn, corresponds to the frequency of the external field.

B. Polarized wave functions

As in earlier work, the perturbed wave function for the scattering states may be expressed in a series of a complete set of bound and continuum wave functions as

$$\Psi(\gamma L M_{L_s}, N+1) = \sum_{j=1}^{m_i} a_j \Phi(\gamma_j L_i S_i; N) \phi_{kl} \\ + \sum_{i=1}^m c_i \Phi(\gamma_i L M_{L_s}; N+1),$$

where the first term represents the coupling of an N -electron target wave function $\Phi(\gamma_j L_i S_i; N)$ with the wave function of the scattering electron to form an eigenstate of total magnetic quantum number M_{L_s} . The second term is the sum of $(N+1)$ -electron bound-state configurations with the same symmetry $L_s M_{L_s}$ and are included for polarization. The polarized orbitals are constructed by solving the coupled integro-differential equations of the form

$$\left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] P_i(r) \\ = \frac{2}{r} [Y_i(r)P_i(r) + X_i(r) + I_i(r)] + \sum_{i'} \epsilon_{ii'} P_{i'}(r)$$

by an iterative method as described in detail earlier [7].

The boundary conditions satisfied by the bound radial functions are

$$P_i(r) \underset{r \rightarrow 0}{\sim} r^{l+1}, \quad P_i(r) \underset{r \rightarrow \infty}{\sim} 0.$$

The radial functions for the scattering orbital for $l=0$ satisfy the conditions

$$P_i(r) \underset{r \rightarrow 0}{\sim} r^{l+1}, \quad P_i(r) \underset{r \rightarrow \infty}{\sim} A \sin(kr - l\pi/2 + \delta_l).$$

For $k^2=0$ and at large r , the s -wave radial function satisfies the condition

$$P_i(r) \sim A'(r-a),$$

where a is the scattering length.

At zero and low energies the polarization of the target atom by the scattering electron is very strong. As a result, all the configurations which account for dipole polarization are considered in the expansion of the scattering function. These configurations are generated by single replacement of the target orbitals by the excited bound orbitals responsible for dipole polarization. The excited bound orbitals, called the polarized orbitals, are obtained by optimizing both bound and continuum orbitals simultaneously at each kinetic energy of the scattering electron. These polarized orbitals, which form the polarized states, are then used to obtain the frequency-dependent dipole polarizabilities.

III. RESULTS

In our earlier paper the application of the MCHF method to the calculation of the static dipole polarizabilities for closed-shell atoms was discussed [8]. In these calculations polarized orbitals were calculated by optimizing the bound and continuum orbitals at zero kinetic energy of the scattering electron and hence at $\omega=0$ of the applied field. The present paper deals with the calculation of the frequency-dependent polarizabilities of an open-shell atom, as for example, atomic oxygen. In this case the ground state $2s^2 2p^4 \ ^3P$ of oxygen atom was determined in the Hartree-Fock approximation [9]. The polarized orbitals were produced by expanding the scatter-

TABLE I. Excited states of oxygen (ground state $1s^2 2s^2 2p^4 \ ^3P$).

Transition	Configuration	LS states
$2p \rightarrow n_i d$	$1s^2 2s^2 2p^3(^4S)n_i d$	3D
	$1s^2 2s^2 2p^3(^2D)n_i d$	$^3S, ^3P, ^3D$
	$1s^2 2s^2 2p^3(^2P)n_i d$	$^3P, ^3D$
$2p \rightarrow n_i s$	$1s^2 2s^2 2p^3(^4S)n_i s$	3S
	$1s^2 2s^2 2p^3(^2D)n_i s$	3D
	$1s^2 2s^2 2p^3(^2P)n_i s$	3P
$2s \rightarrow n_i p$	$1s^2 2s 2p^4(^4P)n_i p$	$^3S, ^3P, ^3D$
	$1s^2 2s 2p^4(^2P)n_i p$	$^3S, ^3P, ^3D$
	$1s^2 2s 2p^5$	3P

TABLE II. Energy differences and dipole matrix elements for (a) $2p \rightarrow nd$ transitions, (b) $2p \rightarrow ns$ transitions, and (c) $2s \rightarrow np$ transitions.

(a)						
n	$2s^2 2p^3(^2D)nd^3S$		$2s^2 2p^3(^2D)nd^3P$		$2s^2 2p^3(^3P)nd^3P$	
	ΔE_k	D_k	ΔE_k	D_k	ΔE_k	D_k
3	1.072 63	1.104 46	1.043 54	1.656 70	1.066 00	0.956 494
4	1.236 14	0.200 95	1.217 34	0.301 43	1.260 37	0.174 028
n	$2s^2 2p^3(^4S)nd^3D$		$2s^2 2p^3(^2D)nd^3D$		$2s^2 2p^3(^2P)nd^3D$	
	ΔE_k	D_k	ΔE_k	D_k	ΔE_k	D_k
3	0.961 89	2.208 93	0.998 18	1.461 07	1.097 65	1.656 70
4	1.124 04	0.401 90	1.188 11	0.265 83	1.281 408	0.301 43
(b)						
n	$2s^2 2p^3(^2D)ns^3S$		$2s^2 2p^3(^2P)ns^3P$		$2s^2 2p^3(^2D)ns^3D$	
	ΔE_k	D_k	ΔE_k	D_k	ΔE_k	D_k
3	0.459 15	0.857 08	0.612 75	0.742 26	0.532 10	0.958 25
4	1.083 15	0.296 37	1.213 92	0.256 66	1.133 26	0.331 35
(c)						
n	$2s 2p^4(^4P)np^3S$		$2s 2p^4(^2P)np^3S$		$2s 2p^4(^4P)np^3P$	
	ΔE_k	D_k	ΔE_k	D_k	ΔE_k	D_k
3	1.030 43	0.114 98	1.496 88	0.081 30	1.078 35	0.199 15
4	1.327 74	0.204 63	1.784 97	0.144 70	1.452 31	0.354 43
n	$2s 2p^4(^2P)np^3S$		$2s 2p^4(^4P)np^3D$		$2s 2p^4(^2P)np^3D$	
	ΔE_k	D_k	ΔE_k	D_k	ΔE_k	D_k
3	1.477 76	0.140 82	1.025 28	0.257 10	1.481 17	0.181 79
4	1.737 69	0.250 62	1.318 92	0.457 57	1.746 15	0.323 55
$2s 2p^5^3P: \Delta E_k = 0.626 98, D_k = 1.638 38$						

ing wave function in terms of configurations involving the single replacement of the target orbitals according to $2s \rightarrow np$ and $2p \rightarrow n'd, n's$. Ninety-eight configurations were used in the distorted-wave-function expansion for the continuum states. The orbitals np , $n's$, and $n'd$ were varied simultaneously with the continuum electron of

zero angular momentum at each kinetic energy of the electron. The calculations were performed for the kinetic energies of the scattering electron corresponding to the frequency from $\omega=0$ to 0.5 at an interval of 0.05. For the calculation of the frequency-dependent polarizability, the polarized orbitals generated at each ω through the ex-

TABLE III. Frequency-dependent polarizabilities in a.u.

ω	With wave functions optimized at $\omega=0$			With wave functions optimized at each ω		
	$\alpha(M_L=0)$	$\alpha(M_L=\pm 1)$	$\alpha(\omega)$	$\alpha(M_L=0)$	$\alpha(M_L=\pm 1)$	$\alpha(\omega)$
0.00	5.1704	5.4210	5.3375	5.1704	5.4210	5.3375
0.05	5.1968	5.4420	5.3610	5.1890	5.4385	5.3553
0.10	5.2760	5.5108	5.4325	5.2301	5.4735	5.3924
0.15	5.4180	5.6229	5.5586	5.3230	5.5570	5.4790
0.20	5.6406	5.8073	5.7517	5.4519	5.6498	5.5838
0.25	5.9808	6.0581	6.0323	5.7850	5.8885	5.8540
0.30	6.5200	6.4100	6.4467	6.3630	6.2405	6.2813
0.35	7.4815	6.9144	7.1034	7.6826	6.8442	7.1237
0.40	9.7812	7.5641	8.3031	12.9115	7.4891	9.2966
0.45	33.1585 ^a	8.9482	17.0183	7.1645	7.9848	7.7114
0.50	2.9788	12.1548	9.0961	8.4402	9.5165	9.1577

^aClose to $2p \rightarrow 3s$ pole.

citation $n = n' = 3, 4$ were used. These polarized orbitals were sufficient to obtain good convergence. It is found that higher values of n and n' make a negligibly small contribution to the frequency-dependent polarizabilities. No allowance was made for the polarization of the 1s electrons since their contributions to the frequency-dependent polarizabilities are known to be very small. Major contributions come from the transitions $2p \rightarrow n'd$ with $n' = 3$ and 4. The frequency-dependent polarizabilities are also calculated with the polarized orbitals evaluated at zero kinetic energy and compared with the results obtained from orbitals evaluated at nonzero kinetic energy.

For atomic oxygen the results are presented for its ground state $2s^2 2p^4 \ ^3P$. With this initial state the only possible states which can be reached by a dipole transition have $L_s = 0, 1, 2$ corresponding to $^3S, ^3P$, and 3D excited states of the atom. The permitted values of M_L and M_L' are 0 and ± 1 . The couplings which are possible from these transitions and which have finite dipole matrix elements are given in Table I. In Table II are given the energy differences and the corresponding dipole matrix elements D_k ($\equiv |\langle L | M_1 | n' L_s \rangle|$) calculated with polarized orbitals, evaluated at zero kinetic energy of the scattered electron, for all possible final states making the dipole transition.

Table III presents results for frequency-dependent po-

larizabilities for different values of magnetic quantum numbers calculated with polarized orbitals evaluated at different frequencies, together with values determined with polarized orbitals obtained at zero frequency. The results are also presented for their average values, which are obtained according to the relation

$$\alpha(\omega) = \frac{1}{3} [\alpha(\omega, M_L = 0) + \alpha(\omega, M_L = +1) + \alpha(\omega, M_L = -1)] .$$

It is seen that there is an increase in the $2p \rightarrow n's$ contribution as we approach the pole due to $2p \rightarrow 3s$ excitation for $\alpha(\omega, M_L = 0)$. It is also observed that $\alpha(\omega)$ fluctuates very rapidly in the regions where there are poles, as expected. We compare present values of $\alpha(\omega)$ for different magnetic quantum numbers at selected values of ω with other accurate theoretical calculations in Table IV. The agreement is very good except at $\omega = 0.4$, where the differences are slightly higher. The values obtained with polarized orbitals evaluated at zero kinetic energy are also displayed within the parentheses. To determine the accuracy of the present calculation, the present results are compared with the accurate experimental results of Alpher and White [6], who measured the static dipole polarizability of atomic oxygen and also the specific refrac-

TABLE IV. Comparison of theoretical and experimental polarizabilities $\alpha(\omega)$ in a.u. The numbers in parentheses are calculated using orbitals optimized at $\omega = 0$.

	$M_L \backslash \omega$	ω				
		0.0	0.10	0.20	0.30	0.40
	0					
Present		5.1704	5.2301 (5.2760)	5.4519 (5.6406)	6.3630 (6.5200)	12.9115 ^a (9.7812)
Kelly (Ref. [1])		5.1910	5.320	5.792	7.192	3.8400
Allison, Burke, and Robb (Ref. [2])		5.0119	5.1368	5.5807	6.5601	1.6045
	± 1					
Present		5.4210	5.4735 (5.5108)	5.6498 (5.8073)	6.2405 (6.4100)	7.4891 (7.5641)
Kelly (Ref. [1])		5.3930	5.4940	5.8290	6.5320	8.0860
Allison, Burke, and Robb (Ref. [2])		5.3023	5.4044	5.8461	6.2196	9.2676
	Total					
Present		5.3375	5.3924 (5.4325)	5.5838 (5.7517)	6.2813 (6.4467)	9.2966 (8.3031)
Kelly (Ref. [1])		5.326	5.4360	5.817	6.752	6.671
Allison, Burke, and Robb (Ref. [2])		5.2055	5.3152	5.7576	6.3331	6.7133

^aClose to $2p \rightarrow 3s$ pole.

TABLE V. Comparison of static dipole polarizabilities of atomic oxygen in \AA^3 .

		$\alpha(\omega=0)$	
Theory	Present	0.791	
	Dalgarno and Parkinson (Ref. [3])	0.89	
	Kelly (Ref. [1])	0.789	
	Allison, Burke, and Robb (Ref. [2])	0.77	
	Henry (Ref. [4])	0.769	
	Lan, Le Dourneuf, and Burke (Ref. [10])	0.747	
	Stevens and Billingsley (Ref. [11])	0.69	
	Burke and Robb (Ref. [12])	0.619	
	Experiment	Alpher and White (Ref. [6])	0.77±0.06

tivity of atomic oxygen at several wavelengths. In Table V we compare the static dipole polarizability of atomic oxygen with experiment and other theoretical results. The present result agrees very well with experiment and with other accurate calculations. The theoretical and experimental values for the specific refractivities of atomic oxygen are compared in Table VI. The specific refractivity K is calculated from the relation

$$K = 2\pi\alpha(\omega)/M,$$

where $\alpha(\omega)$ is given in \AA^3 and M is the mass of an oxygen atom in grams. The present results of specific refractivity agree reasonably well with the available experimental and other theoretical results.

IV. CONCLUSION

We have described in this paper the multiconfiguration Hartree-Fock method for the calculation of the frequency-dependent polarizability of open-shell atoms. Excellent agreement between our results for calculations for atomic oxygen with experiment and other accurate theoretical calculations indicates that the MCHF method is a powerful and sophisticated tool for determining accurate frequency-dependent atomic dipole polarizabilities. The major motivation for our work was to produce frequency-dependent polarized orbitals which could be used for the calculation of atomic dipole polarizabilities. In fact, the MCHF method is more efficient and reliable

TABLE VI. Comparison of specific refractivities K of atomic oxygen. The numbers in parentheses are calculated using orbitals optimized at $\omega=0$.

Wavelength ω (a.u.)	4122 (0.1106)	4515 (0.1009)	5446 (0.0837)
Theory			
Present	0.1874 (0.1891)	0.1869 (0.1882)	0.1864 (0.1874)
Kelly (Ref. [1])	0.1916	0.1905	0.1893
Allison, Burke, and Robb (Ref. [2])	0.1852	0.1843	0.1827
Experiment			
Alpher and White (Ref. [6])	0.19±0.02	0.17±0.02	0.18±0.02

than any other existing calculation of the frequency-dependent polarizability of atoms since it determines frequency-dependent polarized orbitals completely ab initio by optimizing both bound and continuum orbitals simultaneously at each kinetic energy of the continuum electron, which in turn, corresponds to the frequency of the external field, through the configuration-interaction procedure. Moreover, polarization of an atom in a frequency-dependent external field have been taken into account in a sophisticated and straightforward way more accurately in the present method than in any other existing methods. Because our approach relies on frequency-dependent polarized orbitals which are generated as a natural consequence of the solution of the Schrödinger equation through the minimization procedure at each frequency, the method is completely general and can be applied to any atom. It should be mentioned that the other theoretical methods listed in Table V may also be applied to any atom, but the results would not be as accurate as would be obtained by the present method. Finally, since the experimental values of the specific refractivity K are given at smaller values of ω , measurement of K at larger values of ω are desirable to check the accuracy of the calculations.

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