individual rotational details are badly overlapped, but which contains a great deal more information than would a simple band contour display. Although some results have been obtained with these procedures, they are of a preliminary nature and will be reported later.

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Fully Coupled Hartree-Fock Calculations of the Refractive Index, Dynamic Polarizability, and Verdet Coefficients of Helium, Beryllium, and Neon*

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Fully coupled Hartree-Fock calculations of the refractive index, dynamic polarizability, and Verdet coefficients of He, Be, Ne, and the corresponding 2-, 4-, and 10-electron isoelectronic series are presented. The time-dependent Hartree-Fock perturbation equations are derived and solved using a variational method, in which the zero-order and the perturbed wave functions are represented by analytical functions containing adjustable parameters which are optimized according to the variational technique. The numerical results for both the refractive index and the Verdet coefficients are fitted to polynomials in even powers of $1/\lambda$, where λ is the wavelength. In this work it is found that the computed refractive indices differ from the corresponding experimental values due to Cuthbertson and Cuthbertson by a very nearly constant amount. That is, if the computed dynamic polarizabilities are adjusted so as to equal the experimental polarizability α at zero frequency, then the experimental and theoretical curves of refractive index versus frequency are nearly identical. This adjustment in α is around 5% (for He) and 10% (for Ne) of the experimental static polarizabilities. Finally, the calculated transition frequencies are around 2% too large for He, 17% too large for Ne, and 9% too small for Be.

I. INTRODUCTION

Interest in the theoretical prediction of the refractive index, the dynamic polarizability, and other related time-dependent properties of atomic systems, involving harmonic perturbations, has been revived. This is primarily because of the newly discovered techniques for solving time-dependent problems. Two of the most notable of these methods are the oscillator sum rules which have been extensively exploited by Dalgarno and his co-workers[1] and the vari-

ation-perturbation approach. In this paper the latter approach is used to obtain the refractive index, Verdet coefficients, and the dynamic polarizability for a number of closed-shell atoms.

The usefulness of the variation-perturbation technique in the time-independent problems is quite well known.[2] Thus the natural extension is to construct a similar approach for the time-dependent problem. In 1963 Karplus and Kolker[3] in a pioneering paper first presented a method to solve a time-dependent problem using a variation-perturbation technique. A slightly different but equivalent formulation by Yaris[4] appeared at about the same time.

One of the most important requirements of the conventional perturbation theory is that the solution to the unperturbed problem for the ground state as well as excited states be known. However, as is well known, one cannot obtain exact solutions to the unperturbed problem for any atom except hydrogen. Thus, an important practical requirement of a successful approach is that the perturbation method be able to use only an approximate unperturbed solution and the excited states need not be explicitly obtained. In the time-independent case several approximate methods satisfying these requirements have been formulated.[5] Many of these same methods have been carried over in the time-dependent case. The Hartree-Fock method is one such approximation considered. From the computational as well as purely theoretical points of view, the Hartree-Fock scheme provides us with one of the most widely extendable methods for solving many-body problems. Several Hartree-Fock models have been considered in the past. In the same manner as in the time-independent case there are two classes of schemes of approximations within the Hartree-Fock framework — the uncoupled and the coupled Hartree-Fock ap-

proximations.[6] Thus far extensive time-dependent results have been obtained only for helium and the isoelectronic series using these various approximations.

Recently one of us has presented an alternative formulation to the time-dependent perturbation theory.[7] Following this approach we present a formulation of the time-dependent coupled Hartree-Fock theory for many-electron closed-shell atomic systems. Using this formalism we obtain first-order time-dependent wave functions and the associated time-dependent properties for He, Be, Ne, and the corresponding isoelectronic series. The results for the dynamic polarizability of helium are in close agreement with the previous coupled Hartree-Fock calculations.[8,9]

In the present formulation, as in many other semiclassical treatments of the interaction of radiation with matter, we consider an atom to be subjected to the influence of a plane-polarized electromagnetic radiation represented by a time-dependent vector potential, from which an interaction Hamiltonian can be constructed.[10] Under such harmonic perturbations the time-dependence of the perturbed wave function can be obtained explicitly. This results in considerable simplifications. In Sec. II of this paper we outline our derivation of the time-dependent coupled Hartree-Fock equations, and give expressions from which the index of refraction, Verdet coefficient, and dynamic polarizability are obtained. In Sec. III, the variation method, used to solve the coupled linear integrodifferential equations obtained in Sec. II, is described. The results of our calculations are presented in Sec. IV along with a comparison with the experimental data. Finally Sec. V is a discussion and summary of the results.

II. THEORY

Consider an N-electron closed-shell atom acted upon by plane-polarized electromagnetic radiation. The customary time-dependent Schrodinger equation then becomes:

$$[H^0 + \lambda H^1(\vec{r},t)]\Psi(\vec{r},t) = i\,\partial\Psi(\vec{r},t)/\partial t, \tag{1}$$

where

$$H^0 = \sum_{i=1}^{N} \left[-\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \sum_{j\neq i}\frac{1}{r_{ij}} \right] \tag{2}$$

is the unperturbed Hamiltonian, and

$$H^1(\vec{r},t) = \sum_j h^1(\vec{r}_j, t) \tag{3}$$

is the perturbing Hamiltonian expressed as a sum of one-electron operators.

In the problem we are considering

$$h^1(\vec{r}_1, t) = \tfrac{1}{2}v(r_1)(e^{+i\omega t} + e^{-i\omega t}), \tag{4}$$

where ω is the angular frequency of the incoming electro-magnetic radiation.

We now proceed to solve Eq. (1) within the framework of Hartree-Fock approximation. Following Frenkel[11], Eq. (1) can be derived from a variational equation:

$$\delta \int \Psi^*(\vec{r},t)[H^0 + \lambda H^1(\vec{r},t) - i\frac{\partial}{\partial t}]\,\Psi(\vec{r},t)d\tau = 0, \tag{5a}$$

on which is imposed the condition

$$\frac{\partial}{\partial t} \int \Psi^*(\vec{r},t)\Psi(\vec{r},t)d\tau = 0. \tag{5b}$$

Now if $\Psi(\vec{r},t)$ is completely unrestricted, Eq. (5) will just give us the time-dependent Schrodinger Eq. (1). Otherwise it gives an approximate form. In particular, if we choose $\Psi(\vec{r},t)$ as a single Slater determinant[12] made up of N spin-orbitals, then we will get time-dependent Hartree-Fock equations. Hence we choose:

$$\Psi(\vec{r},t) = (\sqrt{N!})^{-1}||\chi_1(1,t)\chi_2(2,t)\cdots\chi_N(N,t)||\,, \tag{6}$$

where $\chi(i,t)$ is the time-dependent spin-orbital.

To insure the orthonormality of the resulting wave function, we require that Eq. (5) be evaluated together with the following restriction:

$$\int \chi_i^*\chi_j d\tau = \delta_{ij}\,. \tag{7}$$

Using Lagrange's method of undetermined multipliers and taking advantage of the spin-orbit reduction, we get the following orbital equation:

$$[h(1)-i\partial/\partial t - i\sum_{j\neq i}<\chi_j|\partial/\partial t|\chi_j>]\chi_i + \sum_k b_{ki}\chi_k = 0, \tag{8}$$

where b_{ki} are the Lagrange multipliers, and

$$h(1) = -\tfrac{1}{2}\nabla_1^2 - Z/r_1 + \sum_j <\chi_j|(1-P_{12})/r_{12}|\chi_j> +\lambda h^1(1,t). \tag{9}$$

The term $<\chi_j|(1-P_{12})/r_{12}|\chi_j>$ used in Eq. (9) signifies

$$<\chi_j|(1-P_{12})/r_{12}|\chi_j> f(1) = f(1)\int \chi_j^*(2)r_{12}^{-1}\chi_j(2)d\tau_2 - \chi_j(1)\int \chi_j^*(2)r_{12}^{-1}f(2)d\tau_2\,, \tag{10}$$

where $f(1)$ is an arbitrary function of the spin and space coordinates of electron 1.

From Eq. (8) one immediately obtains:

$$\sum_l b_{li}\chi_l = -\sum_l A_{li}\chi_l + i\sum_{j\neq i}<\chi_j|\partial/\partial t|\chi_j>\chi_i\,, \tag{11}$$

where

$$A_{li} = <\chi_l|h(1)-i\partial/\partial t|\chi_i>\,. \tag{12}$$

Substituting Eq. (11) back in Eq. (8) one obtains:

$$[h(1)-i\partial/\partial t]\chi_i = \sum_l A_{li}\chi_l\,. \tag{13}$$

Now since A_{li} is Hermitian we know there exists a unitary transformation which will diagonalize A_{li} and also leave the Eq. (13) invariant.[12] Hence we get the following equation:

$$[h(1)-i\partial/\partial t]\chi_i' = 0\,, \tag{14}$$

where

$$\chi_i' = e^{-i\eta_i(t)}\chi_i'' \tag{15}$$

χ_i'' in Eq. (15) is the set of spin orbitals for which A_{li} in Eq. (13) is diagonal, and

$$\eta_i(t) = \int A_{ii}(t)dt\,. \tag{16}$$

Also $h(1)\chi_i'$ appearing in Eq. (14) is then given by:

$$h(1)\chi_i' = (-\tfrac{1}{2}\nabla_1^2 - Z/r_1)\chi_i' + \sum_j <\chi_j'|r_{12}^{-1}(1-P_{12})\chi_j'>\chi_i' + \lambda h^1\chi_i'\,. \tag{17}$$

We now proceed to obtain the perturbed one-electron Hartree-Fock equations. For this we introduce a perturbation expansion. To simplify the notation, primes on χ_i are dropped in what follows. Then, writing

$$\eta_i = \epsilon_i^0 t + \lambda\eta_i^1(t) + \cdots \tag{18}$$

$$\chi_i = \chi_i^0 + \lambda\chi_i^1 + \cdots\,. \tag{19}$$

and substituting into Eq. (14), we have to zeroth and first order in λ, respectively,

$$[h^0(1)-\epsilon_i^{\,0}]\chi_i^{\,0}(\vec{r})=0 \tag{20}$$

and

$$(h^0(1)-\epsilon_i^{\,0}-i\,\partial/\partial t)\chi_i^{\,1}+(h^1+v^1-\eta_i^{\,1})\chi_i^{\,0}=0. \tag{21}$$

Here $h^0(1)$ is the zeroth-order Hartree-Fock operator,

$$h^0(1)=-\tfrac{1}{2}\nabla_1^{\,2}-Z/r_1+v^0, \tag{22}$$

where

$$v^0=\sum_{j=1}^{N}<\chi_j^{\,0}|r_{12}^{-1}(1-P_{12})|\chi_j^{\,0}>. \tag{23}$$

Also v^1 appearing in Eq. (21) contains coupling terms and is given by:

$$v^1=\sum_{j=1}^{N}[<\chi_j^{\,1}|r_{12}^{-1}(1-P_{12})|\chi_j^{\,0}>+<\chi_j^{\,0}|r_{12}^{-1}(1-P_{12})|\chi_j^{\,1}>]. \tag{24}$$

$\dot{\eta}_i^{\,1}$ appearing in Eq. (21) can very easily be obtained as:

$$\dot{\eta}_i^{\,1}=<\chi_i^{\,0}|h^0-\epsilon_i^{\,0}-i\,\partial/\partial t|\chi_i^{\,1}>+<\chi_i^{\,0}|h^1+v^1|\chi_i^{\,0}>. \tag{25}$$

If the perturbing potential h^1 has odd parity, then $\dot{\eta}_i^{\,1}$ vanishes and we get:

$$(h^0-\epsilon_i^{\,0}-i\,\partial/\partial t)\chi_i^{\,1}+(h^1+v^1)\chi_i^{\,0}=0, \tag{26}$$

as the first-order one-electron time-dependent Hartree-Fock equation. It is of interest to note that Eq. (21) with $\dot{\eta}_i^{\,1}$ defined by Eq. (25) is equivalent to Dalgarno and Victor's[8] result, though the assumptions are slightly different.

Before formulating a variational functional to solve Eq. (26) we first obtain an equivalent equation in terms of the atomic orbitals rather than the spin-orbitals in which it is presently expressed. We define

$$\chi_{2i-1}=\varphi_i\alpha, \text{ and } \chi_{2i}=\varphi_i\beta, \tag{27}$$

where χ's are the spin-orbitals and ϕ's are the atomic orbitals. Clearly then,

$$n=\tfrac{1}{2}N=\text{total number of doubly occupied orbitals.} \tag{28}$$

In terms of these orbitals we can rewrite Eq. (26) as follows:

$$(h_i^{\,0}-\epsilon_i^{\,0}-i\,\partial/\partial t)\varphi_i^{\,1}+<\varphi_i^{\,1}|r_{12}^{-1}|\varphi_i^{\,0}>\varphi_i^{\,0}+(h^1+v_i^{\,1})\varphi_i^{\,0}=0, \tag{29}$$

where

$$h_i^{\,0}=-\tfrac{1}{2}\nabla_1^{\,2}-Z/r_1+\sum_{j\neq i}^{N}[<\varphi_j^{\,0}|(2-P_{12})/r_{12}|\varphi_j^{\,0}>+<\varphi_i^{\,0}|(1+P_{12})/r_{12}|\varphi_i^{\,0}>] \tag{30}$$

and

$$v_i^{\,1}=\sum_{j\neq i}^{N}[<\varphi_j^{\,1}|(2-P_{12})/r_{12}|\varphi_j^{\,0}>+<\varphi_j^{\,0}|(2-P_{12})/r_{12}|\varphi_j^{\,1}>]. \tag{31}$$

If the electric field of the radiation is polarized in the z direction, we have

$$F(t)=\tfrac{1}{2}F_z(e^{i\omega t}+e^{-i\omega t}). \tag{32}$$

The exact form of the perturbation potential necessary to calculate the dynamic polarizability, refractive index, etc., of an atomic system, can then be written as

$$\lambda H^1(r,t)=\lambda\sum_{j=1}^{N}h^1(j,t)=\tfrac{1}{2}F_z\sum_{j=1}^{N}z_j(e^{i\omega t}+e^{-i\omega t}). \tag{33}$$

Since we have assumed the perturbing potential h^1 to be of the harmonic type, we can write:

$$\varphi_i^{~1}(t) = \varphi_{i+}^{~1}(\vec{r})e^{i\omega t} + \varphi_{i-}^{~1}(\vec{r})e^{-i\omega t}. \tag{34}$$

After substituting Eqs. (34) and (4) in Eq. (29), and collecting the coefficients of $e^{i\omega t}$ and $e^{-i\omega t}$, one obtains:

$$(h_i^{~0} - \epsilon_i^{~0} \pm \omega)\varphi_{i\pm}^{~1} + < \varphi_{i\pm}^{~1} | r_{12}^{~-1} | \varphi_i^{~0} > \varphi_i^{~0} + [\tfrac{1}{2}v(r_1) + v_{i\pm}^{~1}]\varphi_i^{~0} = 0 , \tag{35}$$

where

$$v_{i\pm}^{~1} = \sum_{\substack{j \neq i}}^{n} [< \varphi_{j\pm}^{~1} | (2 - P_{12})/r_{12} | \varphi_j^{~0} > + < \varphi_j^{~0} | (2 - P_{12})/r_{12} | \varphi_{j\pm}^{~1} >]. \tag{36}$$

Equations (35) are a set of two coupled, time-independent, inhomogeneous integrodifferential equations. These have to be solved to obtain the first-order steady-state wave function of the system. The variational method that we use to solve these equations is described in Sec. III.

Once we obtain the first-order wave function we can calculate many physical properties of interest such as the index of refraction, optical rotatory power of a dilute medium, etc. We now give the expressions for these various properties in terms of the first-order wave function.

1. Dynamic Polarizability and the Refractive Index

The electric dipole moment P is defined as:

$$P = < \Psi(\vec{r},t) | \sum_i Z_i | \Psi(\vec{r},t) >. \tag{37}$$

Now $\Psi(\vec{r},t)$ can be expressed in a perturbation sequence as follows:

$$\Psi(\vec{r},t) = \Psi^0(\vec{r},t) + \tfrac{1}{2}F_z e^{i\omega t}\Psi_+^{~1} + \tfrac{1}{2}F_z e^{-i\omega t}\Psi_-^{~1} + \text{(higher-order terms)} \tag{38}$$

Substituting Eq. (38) in the expression for P, and keeping terms up to first order in F_z we get:

$$P = < \Psi^0 | \sum_i Z_i | \Psi^0 > + F(t)(< \Psi_+^{~1} | \sum_i Z_i | \Psi^0 > + < \Psi^0 | \sum_i Z_i | \Psi_-^{~1} >) , \tag{39}$$

where $F(t)$ is defined by Eq. (32).

The dynamic polarizability $\alpha(\omega)$ is defined as the coefficient of $F(t)$ in the expansion of the dipole-moment operator. Thus from Eq. (39) we obtain:

$$\alpha(\omega) = < \Psi_+^{~1} | \sum_i Z_i | \Psi^0 > + < \Psi^0 | \sum_i Z_i | \Psi_-^{~1} > \tag{40}$$

In the Hartree-Fock approximation we deal with the atomic orbitals $\phi_{i\pm}^{~1}$ defined by Eq. (27). In terms of these, Eq. (40) for the dynamic polarizability becomes:

$$\alpha(\omega) = -4 \sum_{i=1}^{n} (< \varphi_{i+}^{~1} | Z | \varphi_i^{~0} > + < \varphi_i^{~0} | Z | \varphi_{i-}^{~1} >). \tag{41}$$

In cgs units the refractive index n for a dilute gas is given by

$$n^2 - 1 = 4\pi N\alpha(\omega) , \tag{42}$$

where N is the number of atoms per cubic centimeter at STP.

2. The Verdet Coefficient

It is a well-known fact that when a magnetic field is applied parallel to the direction of linearly polarized radiation incident on a dilute medium, the plane of polarization is rotated. This is the Faraday effect. Unlike the natural rotation (i.e., rotation in the absence of the magnetic field) which occurs in a very special class of media, such as crystals with helical structure, the Faraday effect is quite a general phenomenon. It has been used to study the molecular structure. The Faraday effect is of the first order in the magnetic field strength H. The rotation Θ in a length l is given by the formula:[13]

$$\Theta = VHl. \tag{43}$$

The factor of proportionality V is called the Verdet constant. H. Becquerel first obtained an expression for V, which is commonly used in the experimental work. We will use the Becquerel formula, as given by Van Vleck,[14] for our calculations:

$$V = (e/2mc^2)\lambda\,(\partial n/\partial\lambda)(\text{rad}/\text{Oe cm}). \tag{44}$$

Where λ is the wavelength of the incident radiation, n the mean index of refraction, and e the electronic charge, m is the mass of the electron and c is the velocity of light in vacuum.

For the purpose of comparing our results with the experiment, we express V in the following units (at STP):

$$V = 1.\,007\times10^6(\lambda\,\partial n/\partial\lambda)(\mu\text{min}/\text{Oe cm}). \tag{45}$$

III. METHOD OF COMPUTATION

The differential Eqs. (35) are solved by a variational technique; that is, the $\phi_{i\pm}{}^1$ are varied so as to extremize the functionals $J_\pm(\phi_{i\pm}{}^1)$, which are given by the following:

$$J_\pm(\varphi_{i\pm}{}^1) = <\varphi_{i\pm}{}^1|h_i{}^0-\epsilon_{i\pm}{}^0\,\omega|\varphi_{i\pm}{}^1> + 2<\varphi_{i\pm}{}^1|h^1+v_{i\pm}{}^1|\varphi_i{}^0> + 2<\varphi_{i\pm}{}^1|<\varphi_{i\mp}{}^1|r_{12}{}^{-1}|\varphi_i{}^0>|\varphi_i{}^0>. \tag{46}$$

The zeroth-order Hartree-Fock orbitals $\phi_i{}^0$ used in the calculations are expressed in terms of an analytic basis set.[15] The first-order trial orbitals $\phi_{i\pm}{}^1$ are chosen so as to contain the same angular symmetry terms as $h^1\phi_i{}^0$. The radial part is chosen to be of the form:

$$R_{i\pm}{}^1(r) = \sum_s C_{is}{}^\pm r^{n_{is}}e^{-Z_{is}r}, \tag{47}$$

where $c_{is}{}^\pm$ are the variation parameters and n_{is} and z_{is} are chosen so as to make the functions suitable for representing the first-order orbitals. Similar functions have been used in the time-independent case, among others, by H. Radt.[16] In the time-dependent case, Sengupta and Mukherji[9] have used similar functions to calculate the dynamic polarizability of helium.

Thus the explicit forms for the first-order trial orbitals are:

a) S orbitals $\varphi_{i\pm}{}^1 = R_{i\pm}{}^1(r)Y_{1,\,0}(\theta,\varphi)$ (48a)

b) P_x and P_y orbitals $\varphi_{i\pm}{}^1 = R_{i\pm}{}^1(r)Y_{2,\,\pm1}(\theta,\varphi)$ (48b)

c) P_z orbitals $\varphi_{i\pm}{}^1 = R_{i\pm}{}^1(r)Y_{0,\,0}(\theta,\varphi) + P_{i\pm}{}^1(r)Y_{2,\,0}(\theta,\varphi)$.   (48c)

Here $P_{i\pm}{}^1(r)$ in Eq. (48c) contains variation parameters $D_{is}{}^\pm$ instead of $C_{is}{}^\pm$; that is,

$$P_{i\pm}{}^1 = \sum_s D_{is}{}^\pm r^{n_{is}}e^{-Z_{is}r}. \tag{49}$$

Also $Y_{l,m}(\theta,\phi)$ used in Eqs. (48) are the normalized spherical harmonics.[17]

In the calculation for neon there is one difficulty which is not present in the case of He or Be. This has to do with our method of solving Eqs. (35). As indicated above we use a variational technique to solve these equations. Implicit in this method is the requirement that the first variations $\delta\phi_{i\pm}{}^1$ be all linearly independent.[18] However, because of the ortho-normality relations, $\phi_{i\pm}{}^1$ are not all independent; that is, we have the following relations:

$$<\varphi_{i-}{}^1|\varphi_j{}^0> + <\varphi_i{}^0|\varphi_{j+}{}^1> = 0 \tag{50a}$$

and,

$$<\varphi_{i+}{}^1|\varphi_j{}^0> + <\varphi_i{}^0|\varphi_{j-}{}^1> = 0 \tag{50b}$$

Now, in the case of He and Be, Eqs. (50) are automatically satisfied because of the odd parity of the perturbation potential. In the case of neon, however, there are 4 orthogonality Eqs. (50) that are not automatically satisfied. To impose these requirements we use the Lagrange's method of undetermined multipliers.

Thus we form new functionals:

$$L_\pm(\varphi_{i\pm}{}^1) = J_\pm(\varphi_{i\pm}{}^1) + \sum_{i\neq j}\lambda_{ij}{}^\pm(<\varphi_{i\mp}{}^1|\varphi_j{}^0> + <\varphi_i{}^0|\varphi_{j\mp}{}^1>). \tag{51}$$

The variational condition

$$\delta L_\pm(\varphi_{i\pm}{}^1) = 0 \tag{52}$$

leads to a set of coupled linear inhomogeneous equations which we solve for the variation parameters $C_{is}{}^\pm$ and $D_{is}{}^\pm$.

A FORTRAN program written by the authors is used on an IBM-7044 computer to calculate the matrix elements and then obtain solution to the linear equations. The first-order wave function so obtained is then used to calculate the various physical properties mentioned earlier.

IV. RESULTS

In Tables I–III we present the results of our calculations for He, Be, and Ne. In each of these tables we give the frequency ν of the perturbing electric field and the corresponding values of the dynamic polarizability, and the index of refraction. The range of frequency considered in each case is from $\nu = 0.0$ (static case) to the first transition frequency. In addition, in these tables the wavelength found for the first transition is indicated along with the corresponding experimental result.[19]

The refractive indices for He and Ne have been measured by Cuthbertson and Cuthbertson.[20] Their experimental values appear to differ from our computed results by a very nearly constant amount. Thus Figs. 1 and 2 compare for He and Ne the measured refractive indices with our computed refractive indices, adjusted so as to be equal at zero frequency. That is, the plotted refractive indices correspond to an adjusted dynamic polarizability $\alpha'(\omega)$, where $\alpha'(\omega) = \alpha_{HF}(\omega) + \Delta\alpha(0)$. In this case $\alpha_{HF}(\omega)$ is our computed coupled Hartree-Fock result and $\Delta\alpha(0)$ is the difference between the experimental and coupled Hartree-Fock static polarizabilities. For the case of helium, shown in Fig. 1, $\Delta\alpha(0)$ is around 5% of $\alpha(0)_{exp}$ and for neon $\Delta\alpha(0)$ is about 10% of $\alpha(0)_{exp}$.

Since no experimental values for the refractive indices of Be are available, we compare our calculated values with the configuration interaction calculations of Kolker and Michels.[21] This is shown in Fig. 3.

In the following, our numerical results for n^2-1 are least-squares-fitted to polynomials in even powers of $1/\lambda$. In each case an increasing number of terms is added to the polynomial until it is found that including successively more terms does not improve the fit or appreciably change the coefficients of the polynomial containing fewer terms.

Thus we obtain for:

He: $\quad n^2-1 = 6.6186 \times 10^{-5}[1 + 2.18 \times 10^5\lambda^{-2} + 5.656 \times 10^{10}\lambda^{-4} + 1.596 \times 10^{16}\lambda^{-6} + \cdots]$ (55a)

Li$^+$: $\quad n^2-1 = 9.4872 \times 10^{-6}[1 + 2.887 \times 10^4\lambda^{-2} + 9.515 \times 10^8\lambda^{-4} + 3.37 \times 10^{13}\lambda^{-6} + \cdots]$ (56)

Be^{2+}: $\quad n^2-1 = 2.5971 \times 10^{-6}[1 + 7.339 \times 10^3\lambda^{-2} + 6.388 \times 10^8\lambda^{-4} + \cdots]$ (57)

N^{3+}: $\quad n^2-1 = 1.1196 \times 10^{-4}[1 + 6.561 \times 10^5\lambda^{-2} + 4.639 \times 10^{11}\lambda^{-4} + 3.249 \times 10^{17}\lambda^{-6} + \cdots]$ (58)

Be: $\quad n^2-1 = 2.2844 \times 10^{-3}[1 + 6.495 \times 10^6\lambda^{-2} + 4.259 \times 10^{13}\lambda^{-4} + 2.799 \times 10^{20}\lambda^{-6} + \cdots]$ (59)

B$^+$: $\quad n^2-1 = 5.7027 \times 10^{-4}[1 + 2.064 \times 10^6\lambda^{-2} + 4.464 \times 10^{12}\lambda^{-4} + 9.723 \times 10^{18}\lambda^{-6} + \cdots]$ (60)

C^{2+}: $\quad n^2-1 = 2.2565 \times 10^{-4}[1 + 1.059 \times 10^6\lambda^{-2} + 1.198 \times 10^{12}\lambda^{-4} + 1.367 \times 10^{18}\lambda^{-6} + \cdots]$ (61)

F$^-$: $\quad n^2-1 = 5.1112 \times 10^{-4}[1 + 1.243 \times 10^6\lambda^{-2} + 2.360 \times 10^{12}\lambda^{-4} + 5.298 \times 10^{18}\lambda^{-6} + \cdots]$ (62)

Ne: $\quad n^2-1 = 1.1926 \times 10^{-4}[1 + 1.783 \times 10^5\lambda^{-2} + 4.780 \times 10^{10}\lambda^{-4} + 1.561 \times 10^{16}\lambda^{-6} + \cdots]$ (63a)

Na$^+$: $\quad n^2-1 = 0.4724 \times 10^{-4}[1 + 5.384 \times 10^4\lambda^{-2} + 4.010 \times 10^9\lambda^{-4} + 3.536 \times 10^{14}\lambda^{-6} + \cdots]$ (64)

For He and Ne Eqs. (55a) and (63a) are to be compared with the semiexperimental results of Dalgarno and Kingston.[22]

He: $\quad n^2-1 = 6.927 \times 10^{-5}[1 + 2.24 \times 10^5\lambda^{-2} + 5.94 \times 10^{10}\lambda^{-4} + 1.72 \times 10^{16}\lambda^{-6} + \cdots]$ (55b)

Ne: $\quad n^2-1 = 1.335 \times 10^{-4}[1 + 2.24 \times 10^5\lambda^{-2} + 8.09 \times 10^{10}\lambda^{-4} + 3.56 \times 10^{16}\lambda^{-6} + \cdots]$ (63b)

Finally for He, Be, and Ne the Verdet coefficient results are:

He: $\quad V = 1.454 \times 10^7\lambda^{-2}[1 + 5.189 \times 10^5\lambda^{-2} + 2.196 \times 10^{11}\lambda^{-4} + \cdots]$ (65a)

Be: $\quad V = 1.490 \times 10^{10}\lambda^{-2}[1 + 1.311 \times 10^7\lambda^{-2} + 1.293 \times 10^{14}\lambda^{-4} + \cdots]$ (66)

Ne: $\quad V = 2.6459 \times 10^7\lambda^{-2}[1 + 5.362 \times 10^5\lambda^{-2} + 2.626 \times 10^{11}\lambda^{-4} + \cdots]$ (67a)

Again the results for He and Ne are to be compared with those of Dalgarno and Kingston.[22]

He: $\quad V = 1.564 \times 10^7\lambda^{-2}[1 + 5.31 \times 10^5\lambda^{-2} + 2.30 \times 10^{11}\lambda^{-4} + \cdots]$ (65b)

Ne: $\quad V = 3.013 \times 10^7\lambda^{-2}[1 + 7.23 \times 10^5\lambda^{-2} + 4.77 \times 10^{11}\lambda^{-4} + \cdots]$ (67b)

In Eqs. (55a) through (67b) λ is expressed in Å units, and the Verdet coefficients V in Eqs. (65a) through (67b) are expressed in the units of μ min/Oe cm.

TABLE I. Computed refractive index and dynamic polarizability of helium.[a]

Frequency (a.u.)	Wavelength (Å)	Dynamic polarizability (a.u.)	Refractive index[b] $(n-1) \times 10^8$
0.00	∞	1.322	3309.6
0.01	7257	1.327	3322.0
0.02	3629	1.344	3364.6
0.03	2419	1.373	3437.2
0.04	1814	1.417	3547.4
0.05	1451	1.478	3700.0
0.06	1210	1.562	3910.4
0.07	1037	1.678	4200.8
0.08	907	1.842	4611.3
0.09	806	2.086	5222.2
0.10	726	2.482	6213.5
0.110	660	3.256	8151.2
0.120	605	5.841	14622.5
0.126	575.9	31.05	77731.5
0.1269	571.8	2555.06	6396416.0[c,d]
0.127	571.6	- 520.080	- 1301983.0
0.128	567	- 21.245	- 53185.3

[a]Zero-order Hartree-Fock wave function; E. Clementi, J. Chem. Phys. 38, 996 (1963).
[b]At STP, $N = 2.689 \times 10^{19}$ atoms/cm^3.
[c]Calculated frequency of first transition: 572 Å.
[d]Experimental frequency of first transition; 584 Å; See Ref. 19.

TABLE II. Computed refractive index and dynamic polarizability of beryllium.[a]

Frequency (a.u.)	Wavelength (Å)	Dynamic polarizability (a.u.)	Refractive index[b] $(n^2 - 1) \times 10^2$
0.0	∞	45.624	0.2284
0.008	9071	49.538	0.2480
0.009	8063	50.694	0.2538
0.010	7257	52.053	0.2606
0.012	6047	55.500	0.2788
0.014	5183	60.216	0.3015
0.016	4535	66.770	0.3343
0.018	4032	76.191	0.3815
0.020	3628	90.479	0.4430
0.021	3456	100.679	0.5041
0.022	3299	114.196	0.5718
0.023	3155	132.888	0.6654
0.024	3024	160.330	0.8027
0.025	2903	204.394	1.0234
0.026	2791	286.436	1.4341
0.027	2688	491.938	2.4630
0.028	2592	1933.777	9.6821[c,d]
0.029	2502	- 946.774	- 4.7404

[a]Zero-order Hartree-Fock wave function; E. Clementi, J. Chem. Phys. 38, 996 (1963).
[b]At STP, $N = 2.689 \times 10^{19}$ atoms/cm^3.
[c]Computed first transition wavelength: 2592 Å.
[d]Experimental wavelength of first transition: 2349 Å; See Ref. 19.

TABLE III. Computed refractive index and dynamic polarizability of neon.[a]

Frequency (a.u.)	Wavelength (Å)	Dynamic polarizability (a.u.)	Refractive index[b] $(n-1) \times 10^8$
0.0	∞	2.3820	5963.2
0.01	7257	2.3901	5983.4
0.02	3629	2.4150	6045.8
0.03	2419	2.4581	6153.7
0.04	1814	2.5227	6315.4
0.05	1451	2.6249	6571.3
0.06	1209	2.7408	6861.4
0.07	1037	2.9194	7308.5
0.08	907	3.1815	7964.7
0.09	806	3.6009	9014.6
0.10	726	4.4069	11032.4
0.11	660	6.9338	17358.3
0.112	648	8.3794	20977.2
0.114	637	11.2165	28079.7
0.116	626	19.5271	48884.7
0.118	615	832.1	2083104.0[c,d]
0.120	605	−144.5059	−36176.0

[a]Zero-order Hartree-Fock wave function; E. Clementi, J. Chem. Phys. 38, 996(1963).
[b]At STP, $N = 2.689 \times 10^{19}$ atoms/cm^3.
[c]Computed first transition wavelength: 615 Å.
[d]Experimental wave length of first transition: 736 Å, See Ref. 19.
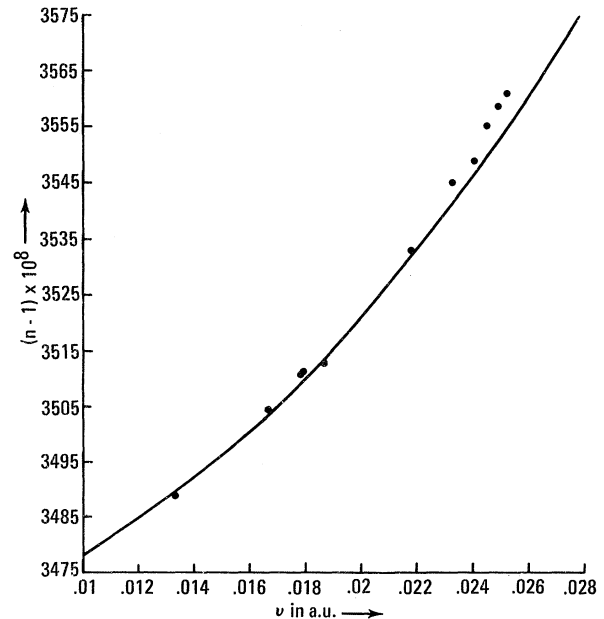

FIG. 1. Plot of refractive index of helium as a function of the frequency. The solid line gives the computed results adjusted so as to equal experimental refractive index at zero frequency. The circles denote the experimental results of Cuthbertson and Cuthbertson, Ref. 20.
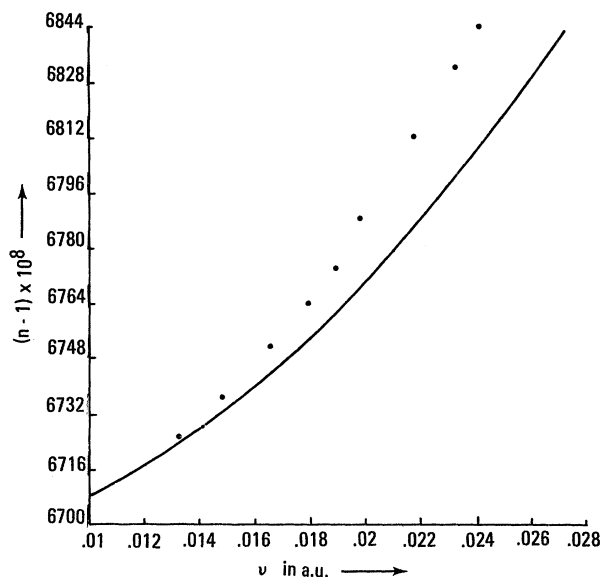
FIG. 2. Plot of refractive index of neon as a function of the frequency. The solid line gives the computed results adjusted so as to equal experimental refractive index at zero frequency. The circles denote the experimental results of Cuthbertson and Cuthbertson, Ref. 20.
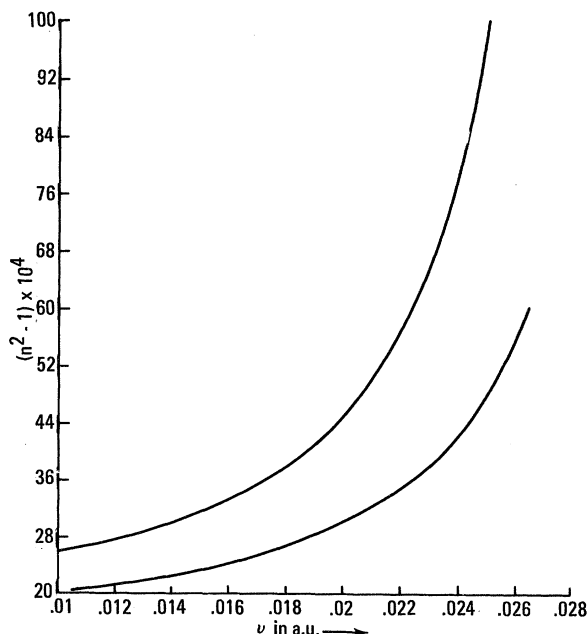

FIG. 3. Plot of refractive index of beryllium as a function of the frequency. The upper curve gives the results obtained in this paper. The lower curve denotes the computed results of Kolker and Michels, Ref. 21.

V. DISCUSSION AND SUMMARY

The results on the static dipole polarizability ($\nu = 0.0$ case) for the atoms under consideration agree very well with the previous[23] coupled Hartree-Fock results. However, as noted in Sec. IV, the agreement with the known experimental values of the static dipole polarizabilities is within the range of about 5–10%. Thus, for example, the experimental polarizability of He, extrapolated from the refractive index data, is reported to be 1.384 a.u.,[22] whereas we obtain 1.322 a.u., the error being approximately 4.5%. It is interesting to note that the discrepancy between our computed values for the refractive indices for the various wavelengths and the corresponding experimental values of Cuthbertson and Cuthbertson for He is also approximately the same as the error in the static polarizability results. We find a similar situation in the case of Ne as well. The experimental static polarizability of Ne is reported to be 2.66 a.u.,[22] whereas we obtain 2.382 a.u., the error being

approximately 10%. Again we find that the difference between the experimental results and our results for the refractive indices of Ne is about 10% also. This fact is well borne out in Figs. 1 and 2, where, as indicated before, we have compared our adjusted theoretical values with those of the corresponding experimental values.

In the case of Be we obtain for the static polarizability a value of 45.62 a.u. This result agrees with the coupled Hartree-Fock result of Dalgarno[24] and that obtained by Kelly[25] using Goldstone perturbation method. However there is some disparity between our value and that of Kolker and Michels. From a configuration interaction calculation, Kolker and Michels obtain 37.5 a.u.[21]

Finally it is of interest to note that the uncoupled Hartree-Fock calculations of Levine and Taylor[26] for Be are in marked disagreement with our results and those of Kolker and Michels at all frequencies.

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Calculation of the Magnetic Moment of Atomic Fluorine

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(Received 15 January 1968)

The atomic g_J factors for the two levels composing the lowest term of atomic fluorine have been calculated utilizing the theory of Kambe and Van Vleck and wave functions resulting from Hartree-Fock treatments of varying accuracy. For the high-accuracy wave functions, the results of our calculation are in exact agreement with the measured $g_J(F^{19}; {}^2P_{\frac{3}{2}})/g_J(H^1; {}^2S_{\frac{1}{2}})$ $=\frac{2}{3}-(497 \pm 1) \times 10^{-6}$, to within the experimental error. The contribution to $g_J(F^{19}; {}^2P_{\frac{3}{2}})$ arising from the Breit interaction is found to amount to 49×10^{-6}. This sizeable contribution, and the excellent agreement obtained, substantiate the validity of the theory and, in particular, of the Breit interaction to the order of α^2. For the upper level, the value $g_J(F^{19}; {}^2P_{\frac{1}{2}})$ $=\frac{2}{3}-(1072 \pm 2) \times 10^{-6}$ is obtained. For this, no experimental test of adequate sensitivity has been made.

I. INTRODUCTION

The various effects affecting the simple atomic Landé g_J factors have been considered by several authors.[1-7] The corrections which are produced arise from the anomalous magnetic moment of the electron,[1,3,8] isotopic effects caused by the motion of the nucleus,[4,5] relativistic and diamagnetic effects,[5,9] and departures from Russell-Saunders coupling.[6] The anomalous magnetic moment is known to the order of α^2, therefore its inclusion in the calculation is readily accomplished. The theories for the isotopic and departures from L-S coupling effects are well established and can be calculated to the accuracy permitted by the available wave functions. Concerning the so-called relativistic and diamagnetic effects, it is convenient to make the following remarks. Abragam and Van Vleck[5] have shown how these effects can be derived from the Darwin-Breit Hamiltonian,[10] which, as it is well known, is of an approximate nature and