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Hartree-Fock Theory of Third-Harmonic and Intensity-Dependent Refractive-Index Coefficients*

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We consider the lowest-order nonlinear contributions to the electric dipole moment induced in closed-shell atomic systems by intense electromagnetic fields. These contributions are comprised of two terms: (i) an intensity-dependent refractive-index coefficient $\chi_{zzzz}(-\omega;\ \omega,\ \omega,\ -\omega)$, and (ii) a third-harmonic coefficient $\chi_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega)$. The problem is formulated within the framework of time-dependent Hartree-Fock perturbation theory. The expressions for $\chi_{zzzz}(-\omega;\ \omega, \omega,\ -\omega)$ and $\chi_{zzzz}(-3\omega;\ \omega,\ \omega,\ \omega)$ contain third- and lower-order frequency-dependent wave functions. It is found possible to eliminate the third-order terms from the expressions for the χ's. A variational method for solving the required second-order integrodifferential equations is proposed. Numerical results for helium are obtained. A zero-frequency Hartree-Fock hyperpolarizability for helium of 35.8 a.u. is obtained which agrees reasonably well with the previous Hartree-Fock calculations of Sitter and Hurst. The Hartree-Fock wave functions give static hyperpolarizability results which are about 17% smaller than more accurate calculations. A "static second-order function" approximation for calculating the χ's is developed and is shown to be useful for obtaining the χ's at low frequencies with a substantial saving in computing effort.

I. INTRODUCTION

The large, monochromatic, coherent electromagnetic fields produced by laser sources have been used in recent years to study experimentally nonlinear electrooptical effects in solids, liquids, and gases. Dilute gases are particularly useful for this work because the effects of interatomic or intermolecular interactions are minimized and therefore the results can be more easily compared with calculations for isolated quantum systems interacting with a radiation field. The results of many radiation-matter experiments depend on the values of nonlinear polarization coefficients. For example, the power flux generated in the third harmonic is proportional to the square of the atomic second hyperpolarizability.[1-3] Also for large field amplitudes the refractive index of a gas is intensity dependent. A third phenomenon manifests itself in Kerr-effect experiments in which the induced electrooptical birefringence is proportional to the atomic hyperpolarizability.[4,5]

In order to describe conveniently nonlinear electrooptical effects theoretically, one must be able to calculate nonlinear, quantum-mechanical, electric-dipole susceptibilities for the atomic and molecular systems of interest. These microscopic results can then be related to the macroscopic polarization via statistical-mechanical methods. This polarization can then be employed as a current source in Maxwell's equations. We thereby have, in principle, a complete description (power flux, phase shifts, etc.) of nonlinear optical effects.[6-8]

In this paper we consider electric-dipole perturbation interactions. Of particular interest from both theoretical and experimental standpoints is the determination of the nonlinear polarization coefficients of spherically symmetric atomic systems produced by a perturbing harmonically time-dependent electric field $F(t)$. The electric-dipole moment of such an atomic system can be expanded in odd powers of $F(t)$, as the coefficients of even powers vanish from parity considerations. In this paper we obtain expressions for the coefficients of $F^3(t)$ in the dipole moment expansion within the fully coupled Hartree-Fock framework. These coefficients give the lowest-order nonlinear contributions to the dipole moment. One of the coefficients, $\chi_{zzzz}(-\omega;\omega,\omega,-\omega)$, is related to an intensity-dependent refractive index, and the other, $\chi_{zzzz}(-3\omega;\omega,\omega,\omega)$, is related to third-harmonic generation. In what follows $\chi_{zzzz}(-\omega;\omega,\omega,-\omega)$ and $\chi_{zzzz}(-3\omega;\omega,\omega,\omega)$ are abbreviated as χ^{ω} and $\chi^{3\omega}$, respectively.

Calculations of χ^{ω}, $\chi^{3\omega}$, and other higher susceptibilities are conveniently handled by time-dependent perturbation theory. Sitz and Yaris[9] calculated the Kerr coefficient and $\chi^{3\omega}$ very accurately for H and He, but their methods are not readily extendable to more complicated systems. Dawes[10] obtained $\chi^{3\omega}$ for the inert gases using a perturbation method in which sums over states are replaced by a single average term. His method is extendable to many-electron atomic systems but the accuracy is not impressive and differs from the Sitz and Yaris helium calculation by about a factor of 4.

We use a time-dependent variation perturbation technique to calculate χ^{ω} and $\chi^{3\omega}$. A variation perturbation method for time-dependent problems has been introduced by Karplus and Kolker.[11] In our development of the theory we include the time-dependent phase factor modifications of Chung.[12] The resulting time-dependent Hartree-Fock theory in many aspects resembles that of Dalgarno and Victor.[13] Inasmuch as the techniques of Sitz and Yaris cannot be readily extended to systems containing more than two electrons, it is a primary goal of this research to determine if the Hartree-Fock scheme can be used to obtain reasonable results for χ^{ω} and $\chi^{3\omega}$ for larger atomic systems as this approach can be extended to larger systems.

In Sec. II the Hartree-Fock equations for an atomic system perturbed by an external time-dependent electric field are developed. We then obtain expressions for χ^{ω} and $\chi^{3\omega}$ which contain frequency-dependent wave functions up to third order. Following a method suggested by Dalgarno and Stewart[14] for time-independent perturbations, and by Epstein[15] for time-dependent perturbations, we eliminate the third-order terms. This makes the computational problem more tractable since we need only calculate wave functions up to second order to obtain χ^{ω} and $\chi^{3\omega}$. The method of solving the second-order equations is described in Sec. III. As a useful test of the theory we calculate χ^{ω} and $\chi^{3\omega}$ for He. In Sec. IV our results for He are presented and a "static second-order function" approximation[9] within the Hartree-Fock framework is described. Finally, Sec. V gives a summary and a brief discussion of the results.

II. THEORY

We consider the interaction of plane-polarized monochromatic electromagnetic radiation with an N-electron atom. The electric field $F(t)$ can be represented by

$$F(t)=\tfrac{1}{2}F_0(e^{i\omega t}+e^{-i\omega t}) \;, \tag{1}$$

where ω is the angular frequency. The Schrödinger equation, expressed in atomic units, for the system is then

$$[H^0(\vec{r})+\lambda H^1(\vec{r},t)-i\partial/\partial t]\,\Psi(\vec{r},t)=0, \tag{2}$$

where

$$H^0=\sum_{j=1}^{N}(-\tfrac{1}{2}\nabla_j^2-Z/r_j+\sum_{j<k}1/r_{jk}) \tag{3}$$

is the Hamiltonian of the unperturbed atom and

$$\lambda H^1=F_0\sum_{j=1}^{N}\tfrac{1}{2}z_j(e^{i\omega t}+e^{-i\omega t}) \tag{4}$$

is the semiclassical, electric-dipole interaction potential expressed as a sum of one-electron operators in the long-wavelength approximation.

We now proceed to solve Eq. (2) within the Hartree-Fock framework. For this we use Frenkel's variational principle[16]:

$$\delta\langle\Psi(\vec{r},t)|\,H^0+\lambda H^1-i\partial/\partial t\,|\Psi(\vec{r},t)\rangle=0 \;, \tag{5}$$

subject to the conservation of probability:

$$\frac{\partial}{\partial t}\,\langle\Psi|\Psi\rangle=0 \;. \tag{6}$$

The time-dependent Hartree-Fock approximation consists of choosing $\Psi(\vec{r},t)$ as a single Slater determinant comprised of N time-dependent spin orbitals $\psi_j(\vec{r}_k,t)$, i.e.,

$$\Psi(\vec{r},t)=(N!)^{-1/2}\|\psi_1(1,t)\psi_2(2,t)\cdots\psi_N(N,t)\|. \tag{7}$$

To ensure that this trial function be normalized we require that the spin orbitals satisfy

$$\langle\psi_j|\,\psi_k\rangle=\delta_{jk} \;. \tag{8}$$

Proceeding in a straightforward manner one obtains the time-dependent one-electron Hartree-Fock equations[17,18]

$$\left(h(1)-i\,\frac{\partial}{\partial t}\right)\psi_j''=A_{jj}\,\psi_j''. \tag{9a}$$

It is convenient to write (9a) as

$$\left(h(1)=i\,\frac{\partial}{\partial t}\right)\psi_j'=0, \tag{9b}$$

where

$$\psi_j'=e^{-i\eta_j(t)}\,\psi_j'', \tag{10}$$

$$h(1)\psi_j'=(-\tfrac{1}{2}\nabla_1^2-Z/r_1)\psi_j' + \textstyle\sum_k\langle\psi_k'|\,(1-P_{12})/r_{12}\,|\,\psi_k'\rangle\,\psi_j'+\lambda h^1\psi_j' \;, \tag{11}$$

and

$$h^1(\vec{r}_1,t)=\tfrac{1}{2}z_1(e^{i\omega t}+e^{-i\omega t}). \tag{12}$$

Here $\eta_j(t)$ is Chung's time-dependent phase factor[12] and the operator $(1-P_{12})/r_{12}$ is defined for any function $f(1)$ by

$$\langle\,\psi_j'|\,(1-P_{12})/r_{12}\,|\,\psi_j'\rangle f(1) =\langle\psi_j'(2)|\,1/r_{12}\,|\,\psi_j'(2)\,\rangle f(1)-\langle\psi_j'(2)|\,1/r_{12}\,|f(2)\rangle\,\psi_j'(1)\;. \tag{13}$$

Here we consider only closed-shell atoms. For such systems it is convenient to convert from the N spin orbitals $\psi_j(\vec{r}_j,t)$ to $n=\tfrac{1}{2}N$ doubly occupied atomic orbitals $\phi_j(\vec{r}_j,t)$:

$$\psi_{2j-1}=\phi_j\alpha \quad\text{and}\quad \psi_{2j}=\phi_j\beta \;, \tag{14}$$

where, to simplify the notation, we have suppressed the primes on the orbitals. The time-dependent Hartree-Fock equations for each atomic orbital are then

$$[h(1)-i\partial/\partial t]\,\phi_j=\dot{\eta}_j\,\phi_j\;, \tag{15}$$

where

$$h(1)\,\phi_j=(-\tfrac{1}{2}\nabla_1^2-Z/r_1)\,\phi_j+v\phi_j+\lambda h^1\,\phi_j \tag{16}$$

and where v is the Fock potential given by

$$v=\textstyle\sum_j\langle\phi_j\,|\,(2-P_{12})/r_{12}\,|\,\phi_j\rangle\;. \tag{17}$$

The remaining problem is then to solve Eq. (15) and use these functions to compute the induced dipole moment. In this paper we use the perturbation technique which involves expanding ψ_j and η_j in a power series in λ. We then have

$$\phi_j(t)=\phi_j^0+\lambda\phi_j^1+\lambda^2\phi_j^2+\lambda^3\phi_j^3+\cdots\;, \tag{18}$$

$$\eta_j\,(t)=\epsilon_j^0\,t+\lambda\eta_j^1+\lambda^2\eta_j^2+\lambda^3\eta_j^3+\cdots\;, \tag{19}$$

and

$$v\,(t)=v^0+\lambda v^1+\lambda^2v^2+\lambda^3v^3+\cdots\;. \tag{20}$$

Substituting Eqs. (18)–(20) into Eq. (15) yields the following hierarchy of integrodifferential equations:

$$(h^0-\epsilon_j^0)\,\phi_j^0=0\;, \tag{21}$$

$$(h^0-\epsilon_j^0-i\partial/\partial t)\,\phi_j^1+(v^1-\dot{\eta}_j^1+h^1)\,\phi_j^0=0\;, \tag{22a}$$

$$(h^0-\epsilon_j^0-i\partial/\partial t)\,\phi_j^2+(v^1-\dot{\eta}_j^1+h^1)\,\phi_j^1+(v^2-\dot{\eta}_j^2)\,\phi_j^0=0\;, \tag{22b}$$

$$(h^0-\epsilon_j^0-i\partial/\partial t)\,\phi_j^3+(v^1-\dot{\eta}_j^1+h^1)\,\phi_j^2+(v^2-\dot{\eta}_j^2)\,\phi_j^1+(v^3-\dot{\eta}_j^3)\,\phi_j^0=0\;, \tag{22c}$$

where

$$h^0=-\tfrac{1}{2}\nabla_1^2-Z/r_1+v^0\;. \tag{23}$$

In Eq. (21) and Eqs. (22),

$$\phi_j^0=\phi_j^0(\vec{r}) \tag{24a}$$

and

$$\phi_j^k=\phi_j^k(\vec{r},t)\;,\quad k=1,2,3. \tag{24b}$$

The $\dot{\eta}_j^k$ are obtained by operating on Eqs. (22) with $\langle\phi_j^0\,|$.

From the form of h^1 [cf. Eq. (12)] one can determine by inspection the explicit time dependence of the solutions to Eqs. (22) as

$$\phi_j^1=\phi_j^1(+1)e^{i\omega t}+\phi_j^1(-1)e^{-i\omega t}\;, \tag{25a}$$

$$\phi_j^2=\phi_j^2(+2)e^{2i\omega t}+\phi_j^2(0)+\phi_j^2(-2)e^{-2i\omega t}\;, \tag{25b}$$

$$\phi_j^3=\phi_j^3(+3)e^{3i\omega t}+\phi_j^3(+1)e^{i\omega t}+\phi_j^3(-1)e^{-i\omega t}+\phi_j^3(-3)e^{-3i\omega t}\;, \tag{25c}$$

where we have separated the space-dependent and time-dependent parts.

It is convenient now to separate the v^l and η_j^l, $l=1,2,3$, into space-dependent and time-dependent parts. Using obvious notation, we have

$$v^1=v^1(+1)e^{i\omega t}+v^1(-1)e^{-i\omega t}\;, \tag{26a}$$

$$v^2=v^2(+2)e^{2i\omega t}+v^2(0)+v^2(-2)e^{-2i\omega t}\;, \tag{26b}$$

$$v^3=v^3(+3)e^{3i\omega t}+v^3(+1)e^{i\omega t}+v^3(-1)e^{-i\omega t}+v^3(-3)^{-3i\omega t}\;, \tag{26c}$$

and

$$\dot{\eta}_j^1=\dot{\eta}_j^1(+1)e^{i\omega t}+\dot{\eta}_j^1(-1)e^{-i\omega t}\;, \tag{27a}$$

$$\dot{\eta}_j^2=\dot{\eta}_j^2(+2)e^{2i\omega t}+\dot{\eta}_j^2(0)+\dot{\eta}_j^2(-2)e^{-2i\omega t}\;, \tag{27b}$$

$$\dot{\eta}_j^3=\dot{\eta}^3{}_j(+3)e^{3i\omega t}+\dot{\eta}_j^3(+1)e^{i\omega t}+\dot{\eta}_j^3(-1)e^{-i\omega t}+\dot{\eta}_j^3(-3)e^{-3i\omega t}\;. \tag{27c}$$

Equations (22) then become the following.

First order:

$$[h^0-\epsilon_j^0\pm\omega]\,\phi_j^1(\pm1)+\tfrac{1}{2}z_1\,\phi_j^0+[v^1(\pm1)-\dot{\eta}_j^1](\pm1)]\,\phi_j^0=0\;. \qquad \text{(28a), (28b)}$$

Second order:

$$[h^0-\epsilon_j^0\pm2\omega]\,\phi_j^2(\pm2)+\tfrac{1}{2}z_1\phi_j^1(\pm1)+[v^1(\pm1)-\dot{\eta}_j^1(\pm1)]\times\phi_j^1(\pm1)+[v^2(\pm2)-\dot{\eta}_j^2(\pm2)]\,\phi_j^0=0\;, \qquad \text{(29a), (29b)}$$

$$[h^0-\epsilon_j^0]\,\phi_j^2(0)+\tfrac{1}{2}z_1[\phi_j^1(+1)+\phi_j^1(-1)]+[v^1(+1)-\dot{\eta}_j^1(+1)]\,\phi_j^1(-1)+[v^1(-1)-\dot{\eta}_j^1(-1)]\times\phi_j^1(+1)+[v^2(0)-\dot{\eta}_j^2(0)]\,\phi_j^0=0\;. \tag{29c}$$

Third order:

$$[h^0-\epsilon_j^0\pm\omega]\,\phi_j^3(\pm1)+\tfrac{1}{2}z_1[\phi_j^2(\pm2)+\phi_j^2(0)]+[v^1(\mp1)-\dot{\eta}_j^1(\mp1)]\,\phi_j^2(\pm2)+[v^1(\pm1)-\dot{\eta}_j^1(\pm1)]\,\phi_j^2(0)+[v^2(\pm2)-\dot{\eta}_j^2(\pm2)]\,\phi_j^1(\mp1)+[v^2(0)-\dot{\eta}_j^2(0)]\,\phi_j^1(\pm1)+[v^3(\pm1)-\dot{\eta}_j^3(\pm1)]\,\phi_j^0=0\;, \qquad \text{(30a), (30b)}$$

$$[h^0-\epsilon_j^0\pm3\omega]\,\phi_j^3(\pm3)+\tfrac{1}{2}z_1\,\phi_j^2(\pm2)+[v^1(\pm1)-\dot{\eta}_j^1(\pm1)]\,\phi_j^2(\pm2)+[v^2(\pm2)-\dot{\eta}_j^2\,(\pm2)]\,\phi_j^1(\pm1)+[v^3(\pm3)-\dot{\eta}_j^3(\pm3)]\,\phi_j^0=0\;. \qquad \text{(30c), (30d)}$$

In this paper we use Clementi's zero-order functions.[19] The first-order functions are those obtained by Kaveeshwar, Chung, and Hurst.[18] The method of solving the second-order equations is given in Sec. III. It is of interest to note that the equations for the jth and the kth orbitals are coupled through the Fock potentials v^l, $l=1,2,3$. Also, $\phi_j^1\,(+1)$ is coupled to $\phi_j^1(-1)$, $\phi_j^2(+2)$ to $\phi_j^2(-2)$, $\phi_j^3(+1)$ to $\phi_j^3(-1)$, and $\phi_j^3(+3)$ to $\phi_j^3(-3)$.

In what follows it is shown that it is not necessary to explicitly obtain the third-order functions. Thus, we first obtain an expression for the induced dipole moment p in the customary way, which contains the third-order functions. We then show from the form of Eqs. (30) that the expressions for p can be reduced to an equation involving only zeroth-, first-, and second-order functions

Following the convention of New and Ward,[1] the frequency-dependent dipole moment is written as a power series in the electric field intensity such that in the limit of zero frequency the coefficient $\alpha(\omega)$ equals the static polarizability and the coefficients χ^{ω} and $\chi^{3\omega}$ each equal the static hyperpolarizability γ:

$$p=\alpha F_0+\tfrac{1}{6}\gamma F_0^3+\cdots\ . \tag{31a}$$

Thus, in the frequency-dependent case,

$$p=\tfrac{1}{2}\alpha(\omega)F_0(e^{i\omega t}+e^{-i\omega t})+\tfrac{1}{24}\chi^{\omega}F_0^3(e^{i\omega t}+e^{-i\omega t})+\tfrac{1}{24}\chi^{3\omega}F_0^3(e^{3i\omega t}+e^{-3i\omega t})\ . \tag{31b}$$

The coefficients $\alpha(\omega)$, χ^{ω}, and $\chi^{3\omega}$ are then obtained by comparing the quantum-mechanical dipole moment with (31b). Thus,

$$p=\langle\psi(\vec{r},t)|\textstyle\sum_j z_j|\psi(\vec{r},t)\rangle=2\sum_j\{F_0[\langle\phi_j^0|z_1|\phi_j^1\rangle+\langle\phi_j^1|z_1|\phi_j^0\rangle]+F_0^3[\langle\phi_j^0|z_1|\phi_j^3\rangle+\langle\phi_j^1|z_1|\phi_j^2\rangle+\langle\phi_j^2|z_1|\phi_j^1\rangle+\langle\phi_j^3|z_1|\phi_j^0\rangle]\}\ , \tag{32}$$

so that

$$\alpha(\omega)=4\textstyle\sum_j[\langle\phi_j^0|z_1|\phi_j^1(+1)+\phi_j^1(-1)\rangle]\ , \tag{33a}$$

$$\chi^{\omega}=32\textstyle\sum_j[\langle\phi_j^0|z_1|\phi_j^3(+1)+\phi_j^3(-1)\rangle+\langle\phi_j^1(-1)|z_1|\phi_j^2(-2)\rangle]+\langle\phi_j^1(+1)|z_1|\phi_j^2(+2)\rangle+\langle\phi_j^1(-1)|z_1|\phi_j^2(-2)\rangle]\ , \tag{33b}$$

$$\chi^{3\omega}=96\textstyle\sum_j[\langle\phi_j^0|z_1|\phi_j^3(+3)+\phi_j^3(-3)\rangle+\langle\phi_j^1(-1)|z_1|\phi_j^2(+2)\rangle+\langle\phi_j^1(+1)|z_1|\phi_j^2(-2)\rangle]\ . \tag{33c}$$

Finally, at zero frequency

$$\alpha=\alpha(\omega)|_{\omega=0} \tag{34a}$$

and

$$\gamma=\chi^{\omega}|_{\omega=0}=\chi^{3\omega}|_{\omega=0}\ . \tag{34b}$$

It can be shown in a number of ways that the coefficients of F_0^3 in the dipole moment expansion can be determined from the second- and lower-order wave functions, i.e., the third-order terms in Eqs. (33b) and (33c) can be eliminated.[9,14,15] Although the procedure is straightforward, it is somewhat tedious. Hence we will indicate the various steps involved and give the final results. First one operates on Eq. (28a) with the bra $\langle\phi_j^3(+1)|$ and on Eq. (28b) with $\langle\phi_j^3(-1)|$. Next Eq. (30a) is operated on with $\langle\phi_j^1(+1)|$ and Eq. (30b) with $\langle\phi_j^1(-1)|$. Upon adding the resulting equations and summing over $j=1$ to n, all of the terms containing third-order functions cancel except

$$\textstyle\sum_j\langle\phi_j^0|z_1|\phi_j^3(+1)+\phi_j^3(-1)\rangle\ ,$$

which is now expressed in terms of functions up to second order. Inserting this result into Eq. (33b) gives χ^{ω} in terms of second- and lower-order functions:

$$\begin{aligned}\chi^{\omega}=64\textstyle\sum_j[&\langle\phi_j^1(+1)+\phi_j^1(-1)|z_1|\phi_j^2(0)\rangle+\langle\phi_j^1(+1)|z_1|\phi_j^2(+2)\rangle+\langle\phi_j^1(-1)|z_1|\phi_j^2(-2)\rangle+\langle\phi_j^1(+1)|v^1(+1)|\phi_j^2(0)\rangle\\&+\langle\phi_j^1(-1)|v^1(-1)|\phi_j^2(0)\rangle+\langle\phi_j^1(+1)|v^1(-1)|\phi_j^2(+2)\rangle+\langle\phi_j^1(-1)|v^1(+1)|\phi_j^2(-2)\rangle\\&+\langle\phi_j^1(+1)|v^2(0)-\dot{\eta}_j^2(0)|\phi_j^1(+1)\rangle+\langle\phi_j^1(-1)|v^2(0)-\dot{\eta}_j^2(0)|\phi_j^1(-1)\rangle\\&+\langle\phi_j^1(+1)|v^2(+2)-\dot{\eta}_j^2(+2)|\phi_j^1(-1)\rangle+\langle\phi_j^1(-1)|v^2(-2)-\dot{\eta}_j^2(-2)|\phi_j^1(+1)\rangle\\&\times\langle\phi_j^1(+1)|v_R^3(+1)|\phi_j^0\rangle+\langle\phi_j^1(-1)|v_R^3(-1)|\phi_j^0\rangle],\end{aligned} \tag{35}$$

where

$$v_R^3(\pm1)=\textstyle\sum_k[\langle\phi_k^1(\pm1)|Q_{12}|\phi_k^2(\pm2)\rangle+\langle\phi_k^1(\mp1)|Q_{12}|\phi_k^2(0)\rangle+\langle\phi_k^2(\mp2)|Q_{12}|\phi_k^1(\mp1)\rangle+\langle\phi_k^2(0)|Q_{12}|\phi_k^1(\pm1)\rangle]$$

(36a), 36b)

are the remaining terms coming from $v^3(\pm1)$, and where $Q_{12}=(2-p_{12})/r_{12}$. If we replace ω by 3ω in Eqs. (28), then a similar procedure can be used to eliminate the third-order terms in $\chi^{3\omega}$, i.e.,

$$\textstyle\sum_j\langle\phi_j^0|z_1|\phi_j^3(+3)+\phi_j^3(-3)\rangle$$

is obtained in terms of second- and lower-order functions. We then have

$$\begin{aligned}\chi^{3\omega}=192\textstyle\sum_j[&\tfrac{1}{2}\langle\phi_j^1(+1)+\phi_j^1(-1)|z_1|\phi_j^2(0)\rangle+\tfrac{1}{2}\langle\phi_j^1(+1)+\phi_j^1(+3)|z_1|\phi_j^2(+2)\rangle+\tfrac{1}{2}\langle\phi_j^1(-1)+\phi_j^1(-3)|z_1|\phi_j^2(-2)\rangle\\&+\langle\phi_j^1(+3)|v^1(+1)|\phi_j^2(+2)\rangle+\langle\phi_j^1(-3)|v^1(-1)|\phi_j^2(-2)\rangle+\langle\phi_j^1(+3)|v^2(+2)-\dot{\eta}_j^2(+2)|\phi_j^1(+1)\rangle\end{aligned}$$

$$+\langle \phi_j^1(-3)\,|\,v^2(-2)-\dot{\eta}_j^2(-2)\,|\,\phi_j^1(-1)\rangle+\langle \phi_j^1(+3)\,|\,v_R^3(+3)\,|\,\phi_j^0\rangle+\langle \phi_j^1(-3)\,|\,v_R^3(-3)\,|\,\phi_j^0\rangle], \tag{37}$$

where

$$v_R^3(\pm 3)=\textstyle\sum_k[\langle \phi_k^1(\mp 1)\,|\,Q_{12}\,|\,\phi_k^2(\pm 2)\rangle+\langle \phi_k^2(\mp 2)\,|\,Q_{12}\,|\,\phi_k^1(\pm 1)\rangle] \qquad \text{(38a), (38b)}$$

are the remaining terms coming from $v^3(\pm 3)$.

III. METHOD OF COMPUTATION

The second-order equations are now solved by a variational technique. First, functionals $J_{\pm 2}[\phi_j^2(\pm 2)]$ and $J_0[\phi_j^2(0)]$ are constructed so as to yield Eqs. (29a), (29b), and (29c), respectively, when varied. These functionals are given by

$$J_{\pm 2}[\phi_j^2(\pm 2)]=\langle \phi_j^2(\pm 2)\,|\,h^0-\epsilon_j^0\pm 2\omega\,|\,\phi_j^2(\pm 2)\rangle+2\langle \phi_j^2(\pm 2)\,|\,\tfrac{1}{2}z_1\,|\,\phi_j^1(\pm 1)\rangle$$
$$+2\langle \phi_j^2(\pm 2)\,|\,v^1(\pm 1)\,|\,\phi_j^1(\pm 1)\rangle+K\langle \phi_j^2(\pm 2)\,|\,v^2(\pm 2)-\dot{\eta}_j^2(\pm 2)\,|\,\phi_j^0\rangle \qquad \text{(39a), (39b)}$$

and

$$J_0[\phi_j^0(0)]=\langle \phi_j^2(0)\,|\,h^0-\epsilon_j^0\,|\,\phi_j^2\ (0)\rangle+2\langle \phi_j^2(0)\,|\,\tfrac{1}{2}z_1\,|\,\phi_j^1(+1)+\phi_j^1(-1)\rangle+2\langle \phi_j^2(0)\,|\,v^1(+1)\,|\,\phi_j^1(-1)\rangle$$
$$+2\langle \phi_j^2(0)\,|\,v^1(-1)\,|\,\phi_j^1(+1)\rangle+K\langle \phi_j^2(0)\,|\,v^2(0)-\dot{\eta}_j^2(0)\,|\,\phi_j^0\rangle\ . \tag{39c}$$

Equations (39) are considerably condensed by introducing the operator K. Thus, in Eqs. (39a), (39b) the expansion of $\langle \phi_j^2(\pm 2)\,|\,v^2(\pm 2)-\dot{\eta}_j^2(\pm 2)\,|\,\phi_j^0\rangle$ [cf. Eqs. (20) and (17)] yields some integrals which are quadratic in $\phi_j^2(\pm 2)$ [e.g., $\langle \phi_j^2(\pm 2)|\langle \phi_j^2(\pm 2)1|r_{12}|\phi_j^0\rangle|\phi_j^0\rangle$] and some terms in which an integral linear in $\phi_j^2(\pm 2)$ is squared [e.g., $\langle \phi_j^2(\pm 2)|\phi_j^0\rangle|^2$]. Then, for the functional to have the desired property, K is defined to assume the numerical value 1 for such terms and a value of 2 for all others. This same convention is used in Eq. (39c).

Next, trial solutions, containing a number of variational parameters, are chosen to approximate the true solutions to Eqs. (29). On substituting these trial solutions into the functionals and on carrying out the variations of $\phi_j^2(\pm 2)$ and $\phi_j^2(0)$, one obtains algebraic equations which when solved for the variational parameters at various frequencies give approximate second-order wave functions.

As a test of the theory we calculate χ^{ω} and $\chi^{3\omega}$ for helium. This is of particular interest because laser experiments have been performed with helium gas.[1,2,4,5] Also, an accurate calculation of some of the frequency dependent nonlinear susceptibilities of He has been performed by Sitz and Yaris.[9] Therefore, we are able to compare the Hartree-Fock results with the more accurate calculations. For helium there is only one atomic orbital so we can omit the orbital subscript. The trial solutions then have the form

$$\phi^2(\pm 2)=\textstyle\sum_k[A_\pm(k)\,Y_{00}(\theta,\phi)+B_\pm(k)Y_{20}(\theta,\phi)]r^{N_k}e^{-Z_k r} \qquad \text{(40a), (40b)}$$

and

$$\phi^2(0)=\textstyle\sum_k[A_0(k)Y_{00}(\theta,\phi)+B_0(k)Y_{20}(\theta,\phi)]r^{N_k}e^{-Z_k r}\ , \tag{40c}$$

where the A's and B's are linear variational parameters. The $Y_{l,m}(\theta,\phi)$'s are the normalized spherical harmonics. The Z_k's in Eqs. (40) are those found[18] previously for $\phi^1(\pm 1)$ and a sufficient number of different N_k's are taken to ensure convergence of the susceptibilities. This method is computationally more efficient than varying the nonlinear parameters Z_k.

We require the atomic orbital $\phi(t)$ of helium to be normalized:

$$\langle \phi(t)\,|\,\phi(t)\rangle=1\ . \tag{41}$$

Thus, substituting the expansion for $\phi(t)$ given by Eq. (18) into Eq. (41), and since

$$\langle \phi^0\,|\,\phi^0\rangle=1\ , \tag{42}$$

we must require that

$$\langle \phi^0\,|\,\phi^1\rangle+\langle \phi^1\,|\,\phi^0\rangle=0 \tag{43}$$

and

$$\langle \phi^0\,|\,\phi^2\rangle+\langle \phi^1\,|\,\phi^1\rangle+\langle \phi^2\,|\,\phi^0\rangle=0\ . \tag{44}$$

Then, substituting Eq. (25a) into Eq. (43) gives

$$\langle \phi^0\,|\,\phi^1(+1)\rangle+\langle \phi^0\,|\,\phi^1(-1)\rangle=0\ , \tag{45}$$

which is automatically satisfied since the angular factor for ϕ^0 is Y_{00} and for $\phi^1(\pm)$ is Y_{10}. On substituting Eq. (25b) into Eq. (44), one obtains

$$\langle \phi^0\,|\,\phi^2(+2)\rangle+\langle \phi^0\,|\,\phi^2(-2)\rangle+\langle \phi^1(+1)\,|\,\phi^1(-1)\rangle=0 \tag{46a}$$

and

$$2\langle \phi^0 | \phi^2(0)\rangle + \langle \phi^1(+1) | \phi^1(+1)\rangle + \langle \phi^1(-1) | \phi^1(-1)\rangle = 0 \,. \tag{46b}$$

The left-hand sides of Eqs. (46) do not automatically vanish. We must impose Eqs. (46) in order to satisfy (44). To do this we use Lagrange's method of undetermined multipliers. Therefore, instead of the functionals $J_{\pm 2}[\phi^2(\pm 2)]$ and $J_0[\phi^2(0)]$, given by Eqs. (39), we construct new functionals

$$\begin{aligned} L_{\pm 2}[\phi^2(\pm 2)] &= J_{\pm 2}[\phi^2(\pm 2)] \\ &\quad + \lambda_2[\langle \phi^0 | \phi^2(+2)\rangle + \langle \phi^0 | \phi^2(-2)\rangle + \langle \phi^1(+1) | \phi^1(-1)\rangle] \end{aligned} \tag{47a), (47b}$$

and

$$\begin{aligned} L_0[\phi^2(0)] &= J_0[\phi^2(0)] + \lambda_0[2 < \phi^0 | \phi^2(0)\rangle \\ &\quad + \langle \phi^1(+1) | \phi^1(+1)\rangle + \langle \phi^1(-1) | \phi^1(-1)\rangle] \,. \end{aligned} \tag{47c}$$

The variational conditions

$$\delta L_{\pm 2}[\phi^2(\pm 2)] = 0 \tag{48a), (48b}$$

and

$$\delta L_0[\phi^2(0)] = 0 \tag{48c}$$

then lead to a set of coupled algebraic equations for the linear variational parameters $A_\pm(k)$ and $B_\pm(k)$ and a set of equations for $A_0(k)$ and $B_0(k)$, respectively.

A Fortran program written by the authors is used to calculate the matrix elements and obtain solutions to the linear algebraic equations. The second-order functions so obtained, and the first-order functions and zeroth-order functions of Refs. 18 and 19, respectively, are then used to calculate χ^ω and $\chi^{3\omega}$.

TABLE I. Intensity-dependent refractive-index coefficient χ^ν and third-harmonic coefficient $\chi^{3\nu}$ for helium.[a]

Frequency (a.u.)	Wavelength (Å)	χ^ν (a.u.)	$\chi^{3\nu}$ (a.u.)
0.000	∞	35.84	35.84
0.005	14 513	36.13	36.71
0.010	7 257	37.05	39.66
0.015	4 838	38.66	45.32
0.020	3 628	41.11	55.50
0.025	2 903	44.64	74.28
0.030	2 419	49.62	113.14
0.035	2 073	56.75	217.16
0.040	1 814	67.27	802.32
0.0426	1 703	74.84	127 117.53
0.0427	1 699	75.17	−31 816.55
0.045	1 613	83.75	
0.050	1 451	112.60	
0.055	1 319	176.36	
0.060	1 209	503.92	
0.0619	1 172	14 700.91	
0.0620	1 170	−19 114.01	

[a] Zero-order Hartree-Fock Ref. 19; first-order Hartree-Fock wave function obtained by method of Ref. 18.

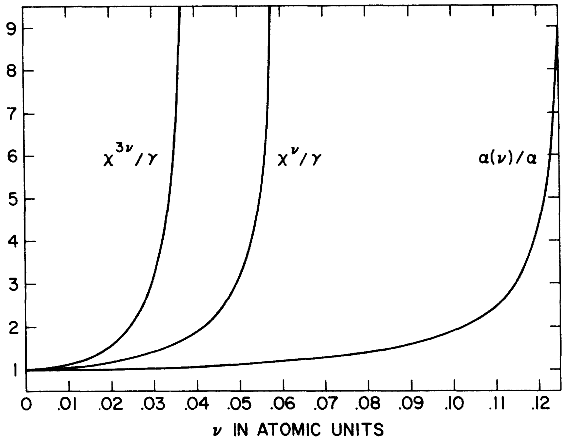

FIG. 1. Intensity-dependent refractive-index coefficient, $\chi^\nu = \chi_{zzzz}(-\nu;\ \nu, \nu, -\nu)$, harmonic coefficient, $\chi^{3\nu} = \chi_{zzzz}(-3\nu;\ \nu, \nu, \nu)$, for helium plotted as ratios to the zero-frequency result $\gamma = 35.8$ a.u. Linear polarizability $\alpha(\nu)$ plotted as ratio to the zero-frequency result $\alpha = 1.32$ a.u.

IV. RESULTS

The numerical results presented in the tables and graph are given as functions of the frequency ν, expressed in atomic units, and is related to ω by the usual relation $\nu = \omega/2\pi$. Thus in Table I, χ^ν is presented for $\nu = 0$ (static field) to $\nu = 0.0620$ a.u. The pole in χ^ν at approximately 0.0620 a.u. corresponds to one-half of the Hartree-Fock energy difference $1s^2 \rightarrow 1s2s$. The experimentally determined[20] wavelength corresponding to the energy difference between the $1s^2$ and $1s2s$ levels is 600.5 Å whereas our calculated value corresponds to 586 Å or about a 3% discrepancy.

In Table I we also present $\chi^{3\nu}$ for $v = 0$ to $\nu = 0.0427$ a.u. The pole at approximately 0.0426 a.u. corresponds to one-third of the transition frequency corresponding to $1s^2 \rightarrow 1s2p$. We calculate the wavelength difference between these two levels to be 567 Å and experiment gives 584 Å or again a 3% discrepancy.

Figure 1 shows plots of χ^ν/γ and $\chi^{3\nu}/\gamma$ as functions of ν, where we represent χ^ν and $\chi^{3\nu}$ at zero frequency by γ. Our result for the zero frequency, or dc, hyperpolarizability γ is 35.8 a.u. The normalized plot of $\chi^{3\nu}/\gamma$ essentially overlaps the result of Sitz and Yaris[9] for helium. This means that the Hartree-Fock result for $\chi^{3\nu}$ is just shifted by a constant factor from their more accurate calculation. The ratio of the frequency-dependent linear polarizability $\alpha(\nu)$ to the zero-frequency re-

TABLE II. Intensity-dependent refractive-index coefficient χ^ν and third-harmonic coefficient $\chi^{3\nu}$ for helium at low frequencies-comparison of static second-order function approximation to frequency-dependent second-order function calculation.

Frequency (a.u.)	χ^ν (a.u.)	χ^ν static approximation (a.u.)	% difference	$\chi^{3\nu}$ (a.u.)	$\chi^{3\nu}$ static approximation (a.u.)	% difference
0.000	35.84	35.84	0.0	35.84	35.84	0.0
0.005	36.13	35.90	0.6	36.71	36.13	1.6
0.010	37.05	36.07	2.6	39.66	37.02	6.7
0.015	38.66	36.35	6.0	45.32	38.69	14.6
0.020	41.11	36.76	10.6	55.50	41.51	25.2

sult, $\alpha = 1.32$ a.u., is also plotted in Fig. 1.

Our Hartree-Fock calculation, employing six linear variational coefficients, yields 35.8 a.u. for the zero-frequency hyperpolarizability of He. Sitter and Hurst[21] recently obtained 36.0 a.u. for the static Hartree-Fock hyperpolarizability of helium by directly solving the Hartree-Fock equations using a self-consistent field technique. Both of these results are seen to be about 17% below the accurate calculations of Sits and Yaris[9] (42.6 a.u.), Grasso, Chung, and Hurst[22] (42.8 a.u.), and Buckingham and Hibbard[23] (43.10 a.u.).

In Table II we present the low-frequency results of the "static second-order function approximation" calculations of χ^ν and $\chi^{3\nu}$ for helium. These results are obtained by inserting the zero frequency functions $\phi^2(\pm 2)$ and $\phi^2(0)$ into the expressions for χ^ν and $\chi^{3\nu}$. For zero frequency,

$$[\phi^2(0)]_{\nu=0} = [2\phi^2(+2)]_{\nu=0} = [2\phi^2(-2)]_{\nu=0} \; .$$

Therefore, in order to perform this calculation we need only obtain $\phi^2(0)$ for zero frequency. The frequency dependence of χ^ν and $\chi^{3\nu}$ is then governed by the frequency dependence of $\phi^1(\pm 1)$. The results are reasonably accurate for optical frequencies.

V. SUMMARY AND DISCUSSION

The discrepancies between the present results and those of Sitz and Yaris[9] are mainly due to the inherent inaccuracies of the Hartree-Fock model. On the other hand the Hartree-Fock calculation possesses the feature of being general in that atoms of a particular type are treated very similarly using the same formalism. Thus the main difficulties in applying the present methods to larger systems result from larger computational problems such as the need to compute more integrals and to solve larger systems of linear equations. The method of Sitz and Yaris is not readily applicable to atoms other than hydrogen and helium.

Despite the errors in the present methods (c.a. 17% for $\nu = 0$) two interesting successes are to be noted. First, the Hartree-Fock formalism when applied to helium predicts the first poles in χ^ν and $\chi^{3\nu}$ to within 3% of the experimental values. Second, the ratio $\chi^{3\nu}/\gamma$ essentially overlaps the more accurate curve of Sitz and Yaris.[9] Thus if one knows γ from static measurements, $\chi^{3\nu}$ can be accurately estimated from the Hartree-Fock frequency-dependent calculations. In this connection, the Hartree-Fock calculations should provide reliable estimates of the error made in comparing measured frequency-dependent susceptibilities with results computed for the static case.

Finally, the static second-order function approximation seems to be very useful in that the results were quite close to the frequency-dependent second-order function calculations of χ^ν and $\chi^{3\nu}$ for low frequencies. The advantage of this method is that we need only solve the static second-order equations and the frequency-dependent first-order equations to obtain reasonably good nonlinear susceptibilities for low frequencies. In addition, the static function approximation is valid for functions more accurate than the Hartree-Fock type. This appears to be a good method for obtaining the frequency-dependent nonlinear susceptibilities of larger atomic systems and possibly molecular systems.

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Off-Diagonal Hyperfine Structure in Sc^{45} †

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The *three* independent coefficients in the magnetic-dipole hyperfine Hamiltonian cannot be determined by measurements of the hfs constants of the *two* atomic states $3d4s^2\ {}^2D_{3/2,\,5/2}$. However, the interaction between these states at a high magnetic field shifts the resonance frequencies for transitions between magnetic substates of either state, and the necessary additional information for evaluating the coefficients may be obtained by observing these frequency shifts. Such measurements, together with more accurate low-field determinations of the hfs constants, lead to ratios of the coefficients in the dipole hfs Hamiltonian in agreement with a recent theoretical prediction. More precise values for the electron g factors are also reported.

I. INTRODUCTION

The lowest term of the neutral scandium atom is ${}^2D$, which arises from the $3d4s^2$ configuration. The atomic ground state is ${}^2D_{3/2}$, and the metastable ${}^2D_{5/2}$ state lies at an excitation[1] of 168.34 cm^{-1}. Both levels are rather pure LS states.

The atomic-beam magnetic-resonance technique was used by Fricke *et al.*[2] in 1959 to measure the hyperfine structure of both the ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states in the only stable isotope (Sc^{45}, for which the nuclear spin is $I=\frac{7}{2}$). In these measurements, the magnetic-dipole and electric-quadrupole hyperfine-interaction constants A and B were measured in each state (diagonal hfs), but direct observation of hyperfine-structure effects due to interactions between the states (off-diagonal hfs) was not attempted. Similar measurements have been made[3] on a number of radioactive isotopes of scandium in order to measure the spin and moments of the nuclear ground states.

More recently it has been shown[4] that the magnetic-dipole hfs Hamiltonian consists of three parts, each with a different tensor character. Since the relative importance of these parts is influenced by such effects as configuration interaction, it is of interest to measure not only the total value of A but also the relative contributions of the three parts separately. Because diagonal hfs studies lead only to A values for the *two* states ${}^2D_{3/2}$ and ${}^2D_{5/2}$, they are not sufficient to identify the *three* contributions to the dipole hfs Hamiltonian separately. Several authors[5] have used off-diagonal hfs studies for such investigations in other