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Index of Refraction of Helium in the Shielding Approximation*

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We have calculated the index of refraction of the helium isoelectronic sequence at low frequencies using the shielding approximation. When compared with experiment for helium, the accuracy is found to be comparable to that typical of the shielding approximation for static properties, about 10%. In an Appendix we extend Brillouin's theorem to time-dependent problems.

I. INTRODUCTION

THE shielding approximation of Dalgarno and Stewart[1] has been extended[2] to the calculation of dynamic properties. In this paper we apply the method to the calculation of $\alpha(\omega)$, the frequency-dependent dipole polarizability, for the helium isoelectronic sequence. From $\alpha(\omega)$ one can then calculate the index of refraction, n, for values of n close to unity, by

$$(n^2-1)=4\pi N_0\alpha\,,$$

where N_0 is given in molecules/unit volume.[3]

The general idea[1] of the method is to calculate first-order corrections to the polarizability of two independent electrons moving in the field of a nucleus of charge ζ. The corrections arise from the Coulomb repulsion between the electrons, and from the difference between ζ and the actual nuclear charge Z. The numerical value of ζ is then determined so as to make these first-order corrections vanish, thus giving a variational flavor to what is otherwise a first-order perturbation calculation.

The shielding approximation is an attractive one: it is conceptually simple, the calculations can be done analytically, it allows one to survey an entire isoelectronic sequence, and in practice[1] the results have been found to be of surprising accuracy (10% or better) for the calculation of static one-electron properties. *Our results show that a similar accuracy may be expected in the calculation of dynamic properties over a range of frequencies.*

To reinforce these remarks, Fig. 1 contains a comparison of our results for He with experiment,[4] and with two other *ab initio* calculations: that of Wheeler[5] who made a detailed analysis of the various oscillator strengths which enter into the familiar second-order perturbation formula for $\alpha(\omega)$, and that of Karplus and Kolker[6] who carried out a rather elaborate numerical, approximate Hartree-Fock calculation. Certainly, in spite of its simplicity, the shielding approximation compares favorably with the other more involved calculations and with experiment.

In Sec. II we give the basic formulas (derivations may be found in Ref. 2). In Sec. III we present our numerical results. In an appendix we prove that if the results of a complete Hartree-Fock calculation were similarly expanded in $Z-\zeta$ and the Coulomb repulsion, then through first order the results would agree with ours, i.e., the Hartree-Fock approximation is accurate through first order.[7]

As will be seen our results are given as power series

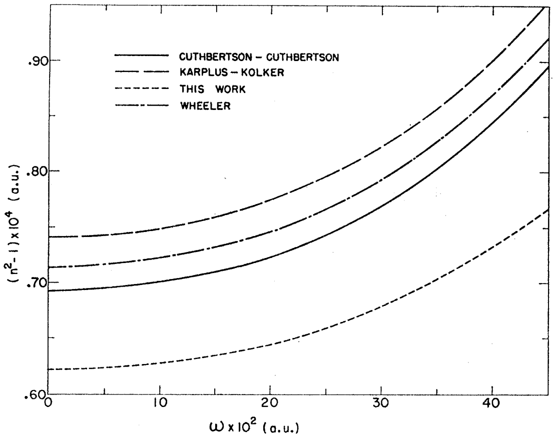

FIG. 1. The refractive index for helium as a function of wavelength.

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[1] A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A257**, 534 (1960).

[2] J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, in *Advances in Quantum Chemistry I* (Academic Press, Inc., New York, 1964), p. 256.

[3] Hartree atomic units are used throughout this paper. In this system the unit of energy, =1 Hartree=27.2097 eV, and the unit of time is $(\hbar^3/me^4)=2.42\times10^{-17}$ sec. Others, in particular Dalgarno and co-workers, use Rydberg atomic units for energy wherein 1 Ry$=\frac{1}{2}$ Hartree.

[4] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A135**, 40 (1932).

[5] J. A. Wheeler, Phys. Rev. **43**, 258 (1933).

[6] M. Karplus and H. J. Kolker, J. Chem. Phys. **39**, 2997 (1963).

[7] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959) has proven the same theorem for the static polarizability $\alpha(0)$.

in ω, arbitrarily stopping with terms of $O(\omega^4)$. Such a representation, though in part dictated by mathematical convenience, seems, more importantly, to be most appropriate to the physical situation. The point is simply that the actual $\alpha(\omega)$ for helium and the zero-order hydrogenic $\alpha(\omega)$ exhibit a series of resonances, and one would not expect our simple, first-order perturbation procedure to work well near either set of resonances.[8] Hence it seemed reasonable to confine our attention to low frequencies.

II. BASIC FUNCTIONS

The basic equations and functions derived from them in the calculation of the dynamic polarizability of helium through first order are given in this section.

$$\alpha(\omega)=-\frac{L_+(\omega)+L_+(-\omega)}{\mathcal{E}^2},$$

where

$$L_+=(\Psi^{(0)},W\Psi_+{}^{(0)})+(\Psi_+{}^{(0)},(V-E^{(1)})\Psi_+{}^{(0)}) \\ +2(\Psi^{(0)},(V-E^{(1)})\theta_+). \quad (1)$$

The functions in Eq. (1) are defined by·

$$(H_0-E^{(0)}+\omega)\Psi_+{}^{(0)}=-W\Psi_+{}^{(0)},$$
$$(H_0-E^{(0)})\theta_+=-W\Psi_+{}^{(0)}+\eta\Psi^{(0)},$$

where

$$\Psi^{(0)}=(\zeta^3/\pi)e^{-\zeta(r_1+r_2)},$$
$$H_0=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-\frac{\zeta}{r_1}-\frac{\zeta}{r_2},$$
$$V=\frac{1}{r_{12}}+\frac{(\zeta-Z)}{r_1}+\frac{(\zeta-Z)}{r_2},$$
$$E^{(1)}=(\Psi^{(0)},V\Psi^{(0)}),$$
$$\eta=(\Psi^{(0)},W\Psi_+{}^{(0)}),$$
$$W=-\mathcal{E}(r_1P_1(\cos\theta_1)+r_2P_1(\cos\theta_2)),$$

with $\mathcal{E}$, the strength of the electric field; r_{12}, the interelectronic distance; r_1 and r_2, the distance from the nucleus to electrons 1 and 2, respectively; and $P_1(\cos\theta_i)$, the ordinary Legendre polynomial. $\Psi_+{}^{(0)}$ and θ_+ were expanded in powers of ω, and then the coefficients of each power of ω were expanded in terms of radial and Legendre functions. Thus, the coefficients of ω^P in $\Psi_+{}^{(0)}$ and θ_+ are of the form

$$\Psi_+{}^{(0,P)}=[f_1{}^{(P)}(r_1)P_1(\cos\theta_1)P_0(\cos\theta_2)+(1\leftrightarrow2)]\Psi^{(0)}$$
$$\theta_+{}^{(P)}=[f_{21}{}^{(P)}(r_1)P_0(\cos\theta_1)P_2(\cos\theta_2) \\ +\tfrac{1}{2}{}_{22}{}^{(P)}(r_1)P_0(\cos\theta_1)P_0(\cos\theta_2) \\ +\tfrac{1}{2}f_3{}^{(P)}(r_1,r_2)P_1(\cos\theta_1)P_1(\cos\theta_2) \\ +(1\leftrightarrow2)]\Psi^{(0)},$$

where $(1\leftrightarrow2)$ means to permute the variables 1 and 2 in the preceding terms. The radial functions are polynomials in the variable(s) designated, the detailed forms being available on request.[9]

III. RESULTS

Our result for the index of refraction is

$$(n^2-1)\times10^4=0.50064\left\{\frac{1}{\zeta^4}\left(9+\frac{b_0}{\zeta}\right)\right. \\ \left.+\frac{\omega^2}{\zeta^8}\left(\frac{319}{6}+\frac{b_2}{\zeta}\right)+\frac{\omega^4}{\zeta^{12}}\left(\frac{297541}{864}+\frac{b_4}{\zeta}\right)\right\},$$

where

$$b_0=(207/16)+36(\zeta-Z)$$
$$b_2=(3983/24)+(1276/3)(\zeta-Z)$$
$$b_4=\frac{4673097941}{2764800}+\frac{297541}{72}(\zeta-Z).$$

The terms b_2 and b_4 are new; all the others can be found in the references of footnote 9.

To determine ζ as a function of ω we follow the procedure outlined in the introduction.[10] Taken literally this would require that

$$b_0+\omega^2(b_2/\zeta^4)+\omega^4(b_4/\zeta^8)=0.$$

However, consistent with the rest of our calculation, we have solved this equation for ζ only through terms of order ω^4. The procedure is straightforward and gives ζ values which range from 1.641 at $\omega=0^8$ to $\zeta=1.629$ at $\omega=0.456$.[11] Figure 1 summarizes our numerical results for helium. Its contents have already been discussed in the introduction.

APPENDIX: AN EXTENSION OF BRILLOUIN'S THEOREM TO TIME-DEPENDENT PROBLEM

Since, as shown in Ref. 1, one can infer the formulas for arbitrary ζ from those for $\zeta=Z$, we may confine ourselves to the latter case. We now recall that the time-dependent Hartree-Fock equations can be derived from the variational principle.[12,13]

$$\left(\delta\Psi_{\mathrm{HF}},\left(H+\frac{1}{i}\frac{\partial}{\partial t}\right)\Psi_{\mathrm{HF}}\right)=0.$$

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[8] One might attempt to deal with frequencies near the resonances within a perturbation framework by explicitly extracting the resonant terms and dealing with them separately.

[9] The $\Psi_+{}^{(0,P)}$ have been given previously by A. Dalgarno and A. E. Kingston, Proc. Roy. Soc. (London) **A259**, 424 (1960) in connection with their calculation of the dynamic polarizability of hydrogen (in detail their $f_{P+1}=[(-1)^P/2^{P+1}]\Psi_+{}^{(0,P)}$). $\theta_+{}^{(0)}$ should appear in the calculation of $\alpha(0)$ for helium by A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. (London) **A247**, 245 (1958) and **A257**, 534 (1960). However, in fact, their quoted $\phi_2{}^{(0)}$ is a spherical average of our $\theta_+{}^{(0)}$; [however, each yields the same result for $\alpha(0)$].

[10] This procedure for determining ζ has the theoretical virtue of being an *a priori* one. *A posteriori* we may remark that one cannot significantly improve agreement with experiment by use of other values for ζ.

[11] The relation between frequency and wave length is λ(Å) $=456/\omega$(atomic units).

[12] L. Brillouin, Act. Sci. Ind., Nos. 71, 159, 160 (1933–4); C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

[13] J. Frenkel, *Wave Mechanics, Advanced General Theory* (Clarendon Press, Oxford, England, 1934), p. 436.

Here H is the total Hamiltonian including Coulomb repulsions and time-dependent external field (which we assume to be turned on adiabatically), Ψ_{HF} is the Hartree-Fock determinant, and $\delta\Psi_{\mathrm{HF}}$ is an allowed variation, i.e., a one-electron excitation of Ψ_{HF}.

Ψ_{HF} satisfies an equation of the form

$$\left(H_{\mathrm{HF}}+\frac{1}{i}\frac{\partial}{\partial t}\right)\Psi_{\mathrm{HF}}=0, \qquad \text{(A1)}$$

whence writing

$$H=H_{\mathrm{HF}}+P,$$

where P explicitly involves only the Coulomb repulsions, and not the external field, we have

$$(\delta\Psi_{\mathrm{HF}},P\Psi_{\mathrm{HF}})=0, \qquad \text{(A2)}$$

We now want to show that (A2) implies that if we write the exact wave function Ψ as

$$\Psi=\Psi_{\mathrm{HF}}+\Delta,$$

that then to first order in P and all orders in the external field, Δ involves no one-electron excitations of Ψ_{HF}. If we can show this, then, as in the static case, it will immediately follow that to all orders in the external field,

$$(\Psi,D\Psi)=(\Psi_{\mathrm{HF}},D\Psi_{\mathrm{HF}})(1+D(P^2))$$

for any one-electron operator D. If we take for D the dipole operator, then we have the result announced in the introduction since one derives $\alpha(\omega)$ from the terms in the expectation value of the dipole operator which are of first order in the field.

To prove that Δ involves no one-electron excitations to first order in P we first note that from

$$\left(H+\frac{1}{i}\frac{\partial}{\partial t}\right)\Psi=0$$

and (A1), it follows that to first order in P, Δ satisfies the equation

$$\left(H_{\mathrm{HF}}+\frac{1}{i}\frac{\partial}{\partial t}\right)\Delta=-P\Psi_{\mathrm{HF}}. \qquad \text{(A3)}$$

Now let us assume we have solved (A1) self-consistently (H_{HF} is in the usual way a functional of Ψ_{HF}) subject to the initial condition that as $t\rightarrow-\infty$, $\Psi_{\mathrm{HF}}\rightarrow\phi_{\mathrm{HF}}e^{-iE_{\mathrm{HF}}t}$, where ϕ_{HF} is the familiar static Hartree-Fock determinant. Having solved (A1) self-consistently, we have a definite operator H_{HF}, and we now make use of the fact that it has a complete orthonormal set of time-dependent solutions,

$$\left(H_{\mathrm{HF}}+\frac{1}{i}\frac{\partial}{\partial t}\right)\Psi_n=0, \quad \Psi_0=\Psi_{\mathrm{HF}}, \qquad \text{(A4)}$$

where as $t\rightarrow-\infty$, $\Psi_n\rightarrow\phi_n e^{-iE_nt}$. Here the ϕ_n are the familiar static virtual Hartree-Fock states.[14] Thus, the Ψ_n are derived from Ψ_{HF} by 1, 2, $\cdots$ electron excitation.

If now we write

$$\Delta=\Sigma a_n(t)\Psi_n,$$

it follows from (A3), (A4) and the orthonormality of the Ψ_n that

$$\frac{1}{i}\frac{da_n}{dt}=-(\Psi_n,P\Psi_{\mathrm{HF}}).$$

From (A2), it then follows that $da_n/dt=0$ if Ψ_n is a one-electron excitation, and since such a_n's are zero at $t=-\infty$ (the usual Brillouin's theorem) it follows that $a_n\equiv0$ for one-electron excitations, which proves the point.

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[14] See, for example, P.-O. Löwdin, Phys. Rev. **97**, 1490 (1953), Sec. 3(a).