PHYSICAL REVIEW VOLUME 107, NUMBER 4 AUGUST 15, 1957

Polarization and Exchange Effects in the Scattering of Electrons from Atoms with Application to Oxygen*†

AARON TEMKIN‡
Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received October 16, 1956)

A method is developed to include polarization effects in low-energy scattering of electrons from atoms, within the Hartree-Fock formalism. This description is different from the usual expansion in terms of the eigenfunctions of the atom. The method associates with each atomic orbital perturbed or polarized parts which also depend parametrically on the coordinates of the scattered particle. When the orbital function of the scattered particle is appropriately antisymmetrized with the total atomic function, augmented in this manner, a set of equations result which, in addition to the no-polarization terms, contain terms coming from the polarized orbitals. By virtue of the antisymmetry, these terms are of two kinds: direct and exchange. The direct terms lead asymptotically to the classical type of polarizability correction which was used by Bates and Massey. The exchange terms constitute a specifically quantum mechanical correction. This method is applied, in a certain approximation, to the s-wave scattering of electrons from oxygen. Only the most important kind of polarized orbital is taken into account. Within this approximation the exchange polarized terms make a contribution of approximately 15% to the cross section.

I. INTRODUCTION

THE Hartree-Fock method was extended to the description of low-energy scattering of electrons from atoms by Morse and Allis in 1933.[1] Their important result was that exchange terms coming from the explicit antisymmetrization of the wave function before substitution into the Schrödinger equation had a significant effect on the low-energy scattering.

One limitation of their wave function, however, is its inability to take account of the reaction of the scattered electron back on the atom; i.e., the method does not seem to include polarization effects. A natural extension of the formalism to include polarization is to expand the total wave function about the eigenfunctions of the atomic system. That is, if one writes the no-polarization wave function as

$$\Psi(1,\cdots,N)=u^{(0)}(1)\Phi_0(2,\cdots,N) \qquad (1.1)$$

(we neglect antisymmetry for the present), where 1 represents the coordinates of the incoming electron, $2,\cdots,N$ the coordinates of the orbital electrons, and Φ_0 the eigenfunction of the atomic system, then one can use a sum

$$\Psi=u^{(0)}(1)\Phi_0(2,\cdots,N)+\sum_{i=1} u^{(i)}(1)\Phi_i(2,\cdots,N) \qquad (1.2)$$

to take account of the effects of polarization.[2] Here Φ_i represent other eigenstates of the atomic system. The $u^{(i)}$ would be determined from the set of equations which can be derived from the substitution of this function into the Schrödinger equation.

The method of expanding about the eigenfunctions of the atomic system is fraught with practical difficulties. One rarely knows the (approximate) eigenfunctions for states beyond the first configuration. If, however, one is restricted to a given configuration, then the different orbital symmetries (configuration interaction) which are generally important in describing polarization are left out. Even with this omission, the inclusion of any more than one function in the form (1.2) gives rise to a calculational problem of the first rank by virtue of the coupled set of integro-differential equations for the $u^{(i)}$ that result. There is, however, a more fundamental objection to this method. Consider, for example, elastic scattering from the ground state of an atom, below the threshold for excitation of its first excited state. In that case the role of the other eigenfunctions of the atom in the expansion (1.2) is strictly a mathematical one. Because of this, one has no guarantee that virtual transitions to states of the continuum do not also play an important part in the description. As a matter of fact, in at least one alternate approach,[3] it was found that the states of the continuum do play a most important role in the description of low-energy scattering. In the present formalism, however, it is unlikely that there is an adequate approximation of the states of continuum (hydrogen excluded) to be useful in an outright expansion of the form (1.2).

From the point of view, therefore, of the effects of the continuum and of configuration interaction, the method of including polarization by expanding about the eigenfunctions of the atom leaves much to be desired. In addition, it leads to a complicated set of simultaneous equations which it would be desirable to avoid. The present paper will be concerned with an alternate method of describing polarization which

---

* This work was supported in part by the Office of Naval Research.

† Now on a Fulbright Fellowship at the University of Heidelberg, Heidelberg, Germany.

‡ Part of this work was submitted to the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933).

[2] This method is discussed more completely by M. J. Seaton, Trans. Roy. Soc. (London) A245, 469 (1953).

[3] M. C. Newstein, Technical Report No. 4, Massachusetts Institute of Technology, 1955 (unpublished).

attempts to improve upon these shortcomings. The method is applied to scattering of electrons from atomic oxygen.

II. BRIEF DESCRIPTION OF THE METHOD

As an alternative to the expansion (1.2), we propose a wave function of the form

$$\Psi=u(1)[\Phi_0(2,\cdots,N)+\Phi^{(\mathrm{pol})}(1;2,\cdots,N)]. \quad (2.1)$$

Our method, then, concerns the construction of the function $\Phi^{(\mathrm{pol})}$. Before discussing this, however, we shall write down a few of the formulas in the application of the Hartree-Fock method to bound-state problems.

Let $H^{(\mathrm{red})}$ be the reduced Hamiltonian of the atomic system. In atomic units,

$$H^{(\mathrm{red})}=\sum_{i=2}^{N}-\nabla_i^2+\sum_{i=2}^{N}\frac{2(N-1)}{r_i}-\sum_{i>j=2}^{N}\sum\frac{2}{r_{ij}}, \quad (2.2)$$

In the Hartree-Fock formalism one assumes a determinantal form for the function Φ_0:

$$\Phi_0=\frac{1}{[(N-1)!]^{\frac{1}{2}}}\det(\varphi_2,\cdots,\varphi_i,\cdots,\varphi_N), \quad (2.3)$$

in which the orbitals φ_i are determined by the condition that the energy be a minimum:

$$\delta\int\Phi_0{}^*H^{(\mathrm{red})}\Phi_0=0. \quad (2.4)$$

This variational principle leads to a set of coupled integro-differential equations for the φ_i, which are:

$$\left[-\nabla^2+\frac{2(N-1)}{r}+\sum_{j(\neq i)=2}^{N}(\mathcal{R}|{}^i{}_j)\right]\varphi_i=\epsilon_i\varphi_i. \quad (2.5)$$

The operator $(\mathcal{R}|{}^i{}_j)$ is defined by:

$$(\mathcal{R}|{}^i{}_j)\varphi_k\equiv\int dx_2\varphi_i{}^*(2)\frac{2}{r_{12}}\varphi_j(2)\varphi_k(1)-\int dx_2\varphi_i{}^*(2)\frac{2}{r_{12}}\varphi_k(2)\varphi_j(1). \quad (2.6)$$

These are the main formulas that we shall need in the subsequent discussion.

The Hamiltonian of the total system of incoming electron plus atom is

$$H=-\nabla_1{}^2+\frac{2(N-1)}{r_1}-\sum_{j=2}^{N}\frac{2}{r_{1j}}+H^{(\mathrm{red})}. \quad (2.7)$$

That part of H which neglects the kinetic energy of the incoming electron can be said to describe the distortion of the atom due to the presence of a *static* electron at a distance $\mathbf{r}_1$ from the origin. The solution of this problem will clearly contain the coordinates $\mathbf{r}_1$ as a parameter; but, otherwise, it can be thought of as a function of the orbital electrons $2,\cdots,N$, not too unlike Φ_0 itself, except that the individual orbitals will be distorted by the presence of the static field of the electron. This is the basic idea of the present method. The deviations of the orbitals from their unperturbed form will be expressed in the function $\Phi^{(\mathrm{pol})}$ of (2.1). Once having obtained this function, we can proceed just as in the no-polarization calculation. That is, we can construct the function Ψ of (2.1) and substitute this form, properly antisymmetrized, into the total Schrödinger equation

$$H\Psi^A=E\Psi^A, \quad (2.8)$$

and reduce this equation to a single integro-differential equation for $u(1)$. The effect of $\Phi^{(\mathrm{pol})}$ will be the addition of terms to the no-polarization equation, however, the scattering phase shift will be determined from the asymptotic form of $u(1)$ in precisely the same way as in the no-polarization case, The succeeding sections are concerned with the mathematical formulation of this program.

III. SOLUTION OF THE STATIC PROBLEM[4]

The basic assumption in the solution of the static problem is based upon the fact that from the point of view of scattering the predominant polarization effects come from the region in which the scattered particle is outside the orbital particles. In other words, we assume that it is a good approximation to replace the interaction terms by the first term in their expansion:

$$\frac{2(N-1)}{r_1}-\sum_{j=2}^{N}\frac{2}{r_{1j}}\cong\sum_{j=2}^{N}\frac{2r_j}{r_1{}^2}\cos\theta_{1j}. \quad (3.1)$$

The approximation (3.1) will be referred to as the dipole approximation. The main justification of this approximation is the argument that near the origin the amplitude of r times the scattered wave is necessarily small by virtue of the boundary condition requirement that it vanish at the origin. This being the case, the predominant interaction will be with the nuclear charge, and the effects of charges in the atomic orbitals induced by polarization will be small in comparison. With this approximation the static Hamiltonian can be written

$$H_I=H^{(\mathrm{red})}+\sum_{j=2}^{N}\frac{2r_j}{r_1{}^2}\cos\theta_{1j}. \quad (3.2)$$

θ_{1j} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_j$. The basic assumption that $r_j<r_1$ allows us to consider the deviation of the static Hamiltonian from the unperturbed Hamiltonian

---

[4] L. Allen, Quarterly Progress Report, Massachusetts Institute of Technology, 1955 (unpublished). I am indebted to L. Allen and R. K. Nesbet for this derivation of the equation for the perturbed orbitals.

$H^{(\text{red})}$ as a small quantity, whose size can be characterized by a parameter λ in the usual sense of perturbation theory. We shall therefore write

$$H_I = H^{(\text{red})} + \lambda \mathcal{V}, \tag{3.3}$$

where $\lambda = 1/r_1^2$ and

$$\mathcal{V} = 2 \sum_{j=2}^{N} r_j \cos\theta_{1j}. \tag{3.4}$$

With the assumption that the perturbation is small, the determinant, Φ_0, of the atomic problem will go over into a determinant Φ_I. The orbitals ψ_i of the new determinant can also be expanded about the parameter λ.

$$\Phi_0 \to \Phi_I = \frac{1}{[(N-1)!]^{\frac{1}{2}}} \det(\psi_1, \cdots, \psi_i, \cdots, \psi_N), \tag{3.5}$$

where

$$\psi_i = \varphi_i + \lambda \varphi_i'. \tag{3.6}$$

The functions φ_i' can be determined by the variational principle for the perturbed function Φ_I.

$$\delta H_{II} = \delta \int \Phi_I^* H_I \Phi_I = 0. \tag{3.7}$$

This leads to the equation

$$\left[-\nabla^2 + \frac{2(N-1)}{r} + \lambda V + \sum_{j(\neq i)=2}^{N} (\Re|{}^{\psi_i}{}_{\psi_j})\right]\psi_i = \epsilon_i'\psi_i, \tag{3.8}$$

where ψ_j in $\Re$ replaces φ_j in the definition (2.6) of $(\Re|{}^{i}{}_{j})$. If one expands the energy ϵ_i' as a power series in λ,

$$\epsilon_i' = \epsilon_i + \lambda \mu_i, \tag{3.9}$$

and one uses the expansion (3.6) of ψ_i, then by equating the various powers of λ, one can obtain the various order equations for the perturbed functions in the expansion of ψ_i. The zeroth order equations is the unperturbed Eq. (2.5). The first order equation can be reduced to the form

$$\left[\frac{2(N-1)}{r} - \nabla^2 + \sum_{j(\neq i)=2}^{N} (\Re|{}^{i}{}_{j}) - \epsilon_i\right]\varphi_i'$$

$$= -V\varphi_i - \sum_{j(\neq i)=2}^{N} [(\Re|{}^{i'}{}_{j}) - (\Re|{}^{i}{}_{j'})]\varphi_i, \tag{3.10}$$

where j' indicates a perturbed orbital φ_j' and j indicates the unperturbed φ_j in the two-body operators $(\Re|{}^{i}{}_{j'})$ and $(\Re|{}^{i'}{}_{j})$. In the reduction of the first order equation to the form (3.10), the odd parity of the perturbation $V = 2r_j \cos\theta_{1j}$ with respect to the coordinate of the orbital electron has been used to show that the first order increment to the energy, μ_i, is zero. If one substitutes the formal solution $\psi_i = \varphi_i + \lambda\varphi_i'$ into the many-particle function Φ_I, one obtains, after expanding the determinant to first order in λ:

$$\Phi_I = \Phi_0 + \lambda \sum_{j=2}^{N} \Phi_j', \tag{3.11}$$

where

$$\Phi_j' = \frac{1}{[(N-1)!]^{\frac{1}{2}}} \det(\varphi_2, \cdots, \varphi_{j-1}, \varphi_j', \varphi_{j+1}, \cdots, \varphi_N). \tag{3.12}$$

The expansion of (3.5) in the form (3.11) is the kind of function we have proposed to describe polarization [see Eq. (2.1)].

An approximate form of the Eq. (3.10) was used by Sternheimer[5] to calculate the polarizability of various closed shell ions and atoms. Actually Sternheimer's equations look quite different from (3.10), but as we shall now show, his equations can be gotten from the rigorous ones by making some not unreasaonble approximations.

Let us replace the quantity

$$\left[\frac{2(N-1)}{r} + \sum (\Re|{}^{i}{}_{j}) - \epsilon_i\right]\varphi_i',$$

on the right-hand side of (3.10) by

$$\frac{\varphi_i'}{\varphi_i}\left\{\left[\frac{2(N-1)}{r} + \sum (\Re|{}^{i}{}_{j}) - \epsilon_i\right]\varphi_i\right\} = \frac{\varphi_i'}{\varphi_i}[\nabla^2 \varphi_i]. \tag{3.13}$$

The equality (3.13) comes from (2.5). This replacement is not an identity because φ_i and φ_i' do not commute with $(\Re|{}^{i}{}_{j})$. More explicitly,

$$\frac{\varphi_i'}{\varphi_i}(\Re|{}^{i}{}_{j})_{j\neq i}\varphi_i = \int dx_2 \varphi_j^*(2) \frac{2}{r_{12}} \varphi_j(2) \varphi_i'(1)$$

$$- \int dx_2 \varphi_j^*(2) \frac{2}{r_{12}} \varphi_i(2) \frac{\varphi_j(1)}{\varphi_i(1)} \varphi_i'(1),$$

whereas the correct expression is

$$(\Re|{}^{i}{}_{j})_{j\neq i}\varphi_i' = \int dx_2 \varphi_j^*(2) \frac{2}{r_{12}} \varphi_j(2) \varphi_i'(1)$$

$$- \int dx_2 \varphi_j^*(2) \frac{2}{r_{12}} \varphi_i'(2) \varphi_j(1).$$

The quantities differ, therefore, only in the exchange terms. One knows from the comparison of Hartree and Hartree-Fock functions that the exchange terms have a small effect compared to the direct terms, and the direct terms are identical in the above approximation. The other approximation that is implicit in Sternheimer's equations is the neglect of the off-diagonal terms on the right hand side of (3.10), i.e., he neglects

---

[5] R. M. Sternheimer, Phys. Rev. 96, 951 (1954).

all terms by $-V\varphi_i$. The fact that the diagonal terms involving the operator $\mathcal{R}$ cancel out in the exact equations would make this approximation, which then rigorously neglects no diagonal terms, also appear reasonable. Sternheimer's equations are thus

$$\left\{-\nabla^2+\left[\frac{1}{\varphi_i}\nabla^2\varphi_i\right]\right\}\varphi_i'=-V\varphi_i, \tag{3.14}$$

where it is understood that the Laplacian in $[\nabla^2\varphi_i]$ does not operate beyond the square bracket.

It should be noted that the method being presented here does not in principle require the approximation of (3.10) by (3.14). However the former equations are a coupled set of integro-differential equations whereas the latter are an uncoupled set of ordinary differential equations. Since it has been our aim to avoid sets of coupled integro-differential equations, Sternheimer's Eqs. (3.14) are very much in the spirit of the method.

The reduction of (3.14) to radial equations is straightforward. Let us write the unperturbed orbital (neglecting the spin of the particle) in the form

$$\varphi_i=u_{nl}(r)Y_{lm}(\Omega), \tag{3.15}$$

where the $Y_{lm}(\Omega)$ are spherical harmonics. The perturbation V is:

$$V=2r_i\cos\theta_{1i}=2r_i\frac{4\pi}{3}\sum_\mu Y_{1\mu}(\Omega_i)Y_{1-\mu}(\Omega_1)(-1)^\mu. \tag{3.16}$$

The product $V\varphi_i$ can be expanded in the form

$$V\varphi_i=2r_iu_{nl}(r_i)\frac{4\pi}{3}\sum_\mu(-1)^\mu Y_{1-\mu}(\Omega_i)Y_{lm}(\Omega_i)Y_{1\mu}(\Omega_i).$$

Using the expansion of a product of spherical harmonics,[6] we find

$$V\varphi_i=2r_iu_{nl}(r_i)\frac{4\pi}{3}\sum_\mu(-1)^\mu Y_{1-\mu}(\Omega_1)$$
$$\times\sum_{l',m'}\left[\frac{3(2l+1)}{4\pi(2l'+1)}\right]^{\frac{1}{2}}(1l00|l'0)$$
$$\times(1l\mu m|l'm')Y_{l'm'}(\Omega_i). \tag{3.17}$$

If now we write the perturbed function φ_i' in a similar form:

$$\varphi_i'=\sum_{l',m'}u_{nl\to l'}(r_i)c_{nl\to l'}{}^{(m\to m')}Y_{l'm'}(\Omega_i)Y_{1m-m'}(\Omega_1), \tag{3.18}$$

then Eq. (3.14), Sternheimer's equation, separates into the radial equations:

$$\left[-\frac{d}{dr^2}+V_{nl\to l'}(r)\right]u_{nl\to l'}(r)=ru_{nl}(r). \tag{3.19}$$

The constants $c_{nl\to l'}{}^{(m\to m')}$ are, from (3.14) to (3.17),

$$c_{nl\to l'}{}^{(m\to m')}=(-1)^{m-m'+1}\left[\frac{16\pi}{3}\left(\frac{2l+1}{2l'+1}\right)\right]^{\frac{1}{2}}$$
$$\times(1l00|l'0)(1lm'-mm|l'm'). \tag{3.20}$$

From the properties of the Clebsch-Gordan coefficient $(1l00|l'0)$, we can conclude that $l'=l\pm1$, where the upper sign holds only for $l=0$. The radial function $V_{nl\to l'}(r)$ is found to be

$$V_{nl\to l'}(r)=\frac{1}{u_{nl}(r)}\left[\frac{d^2}{dr^2}u_{nl}(r)\right]+\frac{l'(l'+1)-l(l+1)}{r^2}. \tag{3.21}$$

From (3.12) and (3.4) we can write down the function $\lambda\Phi_i'$:

$$\lambda\Phi_i'=\sum_{l',m'}c_{nl\to l'}{}^{(m\to m')}\frac{Y_{1m-m'}(\Omega_1)}{r_1^2}\frac{1}{[(N-1)!]^{\frac{1}{2}}}$$
$$\times\det(\varphi_2,\cdots,u_{nl\to l'}Y_{l'm'}\chi(sm_s),\cdots,\varphi_N). \tag{3.22}$$

As a function of the coordinates of the orbital electron, the perturbed orbital has the same spin $\chi(sm_s)$ as the unperturbed function φ_i which it replaces in Φ_0. The total function,

$$\lambda\sum_{i=2}^N\Phi_i',$$

is then a sum in which each orbital is replaced consecutively by all its polarized parts.

Before discussing the solution of the dynamic (scattering) problem, we should like to point out how the perturbed orbitals, φ_i', do contain, at least partially, the effects of both the continuum and configuration interaction. The perturbed angular dependence, $Y_{l'm'}$, of the orbital particles is different from their unperturbed dependence Y_{lm}. In particular the orbital with the highest l goes over into one with an $l'=l+1$, so that the perturbed wave function contains terms of even higher angular asymmetry than the original function. Since this difference is only of one unit, however, this corresponds roughly to a perturbation of some close-lying configuration (configuration interaction). The radial dependence, on the other hand, reflects the effects even of the states of the continuum. This is due to the inhomogeneous nature of Eq. (3.19). The homogeneous solutions of the Sternheimer equations are (approximately) the unperturbed functions $u_{nl}(r)$. Therefore the Green's function for the radial equations (3.19) can be written:

$$G(r,r_0)=-4\pi\sum_{n''l''}{}'\frac{u_{n''l''}(r)u_{n''l''}(r_0)}{\epsilon_{n''l''}-\epsilon_{nl}},$$

where the sum *includes* the states of the continuum.

The solution of the inhomogeneous equation, $u_{nl\to l'}(r)$,

---

[6] J. B. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley and Sons, Inc., New York, 1952), p. 791.

can therefore be written

$$u_{nl\to l'}(r)=-4\pi\sum_{n''l''}{}'\frac{u_{n''l''}(r)}{\epsilon_{n''l''}-\epsilon_{nl}}\int_0^\infty \times u_{n''l''}(r_0)u_{nl}(r_0)r_0dr_0+f_{l,\,l'}(r),$$

where $f_{l,\,l'}(r)$ is some solution of the homogeneous equation. In this form one can see explicitly that the function $u_{nl\to l'}(r)$ does contain to some extent the effects of all states, both bound and continuous.

IV. SOLUTION OF THE SCATTERING (DYNAMIC) PROBLEM

It has already been stated that the solution of the scattering problem is effected in the same way as in the no-polarization calculation with the replacement of the function Φ_0 by $\Phi_0+\Phi^{(\mathrm{pol})}$. However, the solution of Sternheimer's equation together with the dipole approximation implicity restricts the radial coordinate of the orbital electron (which we shall call r_i: $i=2,\cdots,N$) relative to the radial coordinate of the scattering particle (which we shall call r_1). In order to construct a method which is physically and mathematically consistent, yet practicable, it will be necessary to make an additional set of approximations. We shall, therefore, review briefly the Hartree-Fock method as it applies to scattering problems, but with the explicit inclusion of $\Phi^{(\mathrm{pol})}$.

If one assumes no spin-orbit forces, the unperturbed eigenfunction of the atom, which was heretofore called Φ_0, can be labelled $\Phi^A(LM_LSM_S;2,\cdots,N)$. This labeling shows that the function is antisymmetric and an eigenfunction of the total orbital and spin angular momenta of the atom. Let the polarized many-particle wave function, $\lambda\Phi^{(\mathrm{pol})}$, which arises from $\Phi^A(LM_LSM_S)$ in the manner described in (III) be labelled

$$\Phi^{(\mathrm{pol})}(LM_LSM_S;1,2,\cdots,N).$$

In the case of the polarized functions the subscripts do not mean that these functions are likewise eigenfunctions of the various angular momenta of the atomic system. In general they will lose their eigenfunction character with respect to the orbital angular momentum, since the perturbation which gives rise to them is not a rotation invariant with respect to the atomic electrons alone. If, however, one constructs an eigenfunction of the total system including the incoming electron, then the inclusion of $\Phi^{\mathrm{pol}}(LM_LSM_S)$ will not affect this property since the perturbation is a rotation invariant with respect to all particles.

From the point of view of scattering it is convenient to transform to a representation in which the *total* spin and orbital angular momenta are good quantum numbers (we shall label these by $L^{(T)}$, $M_L{}^{(T)}$, $S^{(T)}$, $M_S{}^{(T)}$). Such a combination is

$$\mathcal{Y}_l(L^{(T)}M_L{}^{(T)}S^{(T)}M_S{}^{(T)};1;2,\cdots,N)\equiv\sum_{M_Sm_s}(S\tfrac{1}{2}M_Sm_s|S^{(T)}M_S{}^{(T)})(LlM_Lm|L^{(T)}M_L{}^{(T)})Y_{lm}(\Omega_1)\chi_{sm_s}(1) \times[\Phi^A(LM_LSM_S;2,\cdots,N)+\Phi^{(\mathrm{pol})}(LM_LSM_S;1;2,\cdots,N)]. \quad (4.1)$$

The total wave function may now be written

$$\Psi(L^{(T)}LS^{(T)}S)=\sum_l[4\pi(2l+1)]^{\frac{1}{2}}i^l\frac{u_{lL^{(T)}S^{(T)}}(r_1)}{r_1}\mathcal{Y}_l(L^{(T)}M_L{}^{(T)}SM_S{}^{(T)};1;2,\cdots,N), \quad (4.2)$$

and one which is completely antisymmetric in all coordinates is

$$\Psi^A(L^{(T)}LS^{(T)}S)=\sum_l[4\pi(2l+1)]^{\frac{1}{2}}i^l\sum_{P_c}(-1)^{P_c}\frac{u_{lL^{(T)}S^{(T)}}(r_1)}{r_1}\mathcal{Y}_l(L^{(T)}M_L{}^{(T)}S^{(T)}M_S{}^{(T)};1;2,\cdots,N). \quad (4.3)$$

P_c is a cylic permutation of $1,2,\cdots,N$ and $(-1)^{P_c}$ is $+1$ or -1 according as P_c is an even or odd permutation of $1,2,\cdots,N$.

Let us write the total Hamiltonian defined in (2.7) in the form

$$H(1,\cdots,N)=H^{(\mathrm{red})}(2,\cdots,N)+K(1,2,\cdots,N), \quad (4.4)$$

where $K(1,2,\cdots,N)$ is defined implicitly from (2.7) and (2.2). The Schrödinger equation

$$H\Psi^A(L^{(T)}LS^{(T)}S)=E\Psi^A(L^{(T)}LS^{(T)}S) \quad (4.5)$$

can be reduced to the form

$$\sum_{P_c}(-1)^{P_c}\{K(1,2,\cdots,N)\Psi(L^{(T)}LS^{(T)}S;1,\cdots,N)\} =k^2\Psi^A(L^{(T)}LS^{(T)}S). \quad (4.6)$$

Here k^2 is the energy of the incoming particle in atomic units (Rydbergs); it is related to the total energy E by

$$E=E_{LS}+k^2, \quad (4.7)$$

E_{LS} being the energy of the eigenstates of the atom.

An essential step in the above reduction is the condition

$$H^{(\mathrm{red})}\Psi(L^{(T)}LS^{(T)}S)=E_{LS}\Psi(L^{(T)}LS^{(T)}S). \quad (4.8)$$

In the no-polarization case, the equation is an approximation based on the variational principle for $\Phi^A(LM_LSM_S)$ and the fact that the expectation value of $H^{(\mathrm{red})}$ is E_{LS} (we neglect the difference between this expectation value and the experimental value). With polarization we use the same Eq. (4.8), because the same results hold to first order in λ, if one replaces the unperturbed atomic function by

$$\Phi^{A}(LM_{L}SM_{S})+\Phi^{(\mathrm{pol})}(LM_{L}SM_{S}).$$

This means then that the interaction of the incoming electron with the orbital electrons is taken into account twice (in an approximate way): once in the determination of $\Phi^{(\mathrm{pol})}$, the approximation there being the dipole approximation; and again in Eq. (4.6) via the appropriate terms in K. The approximation here is Eq. (4.8). The interaction K also contains, however, dynamic effects of the incoming particle.

If one multiplies (5.6) on the left by

$$\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,\cdots,N)$$

and[7] integrates over all coordinates except the radial coordinate of particle 1 (which integration we shall denote by $dr_{1}{}^{-1}$ in the integrals below), one obtains the following equation:

$$\begin{aligned}
&\int \mathcal{Y}_{l'}{}^{*}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,\cdots,N)K(1,2,\cdots,N)\sum_{l}[4\pi(2l+1)]^{\frac{1}{2}}i^{l}\frac{u_{lL^{(T)}S^{(T)}}(r_{1})}{r_{1}}\\
&\quad\times\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,\cdots,N)dr_{1}{}^{-1}\\
&\quad-(N-1)\int \mathcal{Y}_{l'}{}^{*}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,\cdots,N)K(2,\cdots,N,1)\sum_{l}[4\pi(2l+1)]^{\frac{1}{2}}i^{l}\frac{u_{lL^{(T)}S^{(T)}}(r_{2})}{r_{2}}\\
&\quad\times\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};2;1,3,\cdots,N)dr_{1}{}^{-1}\\
&\quad=k^{2}\int \mathcal{Y}_{l'}{}^{*}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,\cdots,N)\sum_{l}[4\pi(2l+1)]^{\frac{1}{2}}i^{l}\frac{u_{lL^{(T)}S^{(T)}}(r_{1})}{r_{1}}\\
&\qquad\times\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1,2,\cdots,N)dr_{1}{}^{-1}-(N-1)k^{2}\int \mathcal{Y}_{l'}{}^{*}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};1;2,3,\cdots,N)\\
&\qquad\qquad\times\sum_{l}[4\pi(2l+1)]^{\frac{1}{2}}i^{l}\frac{u_{lL^{(T)}S^{(T)}}(r_{2})}{r_{2}}\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)};2;1,3,\cdots,N)dr_{1}{}^{-1}. \qquad (4.9)
\end{aligned}$$

From (4.1) we see that the function

$$\mathcal{Y}_{l}(L^{(T)}M_{L}{}^{(T)}S^{(T)}M_{S}{}^{(T)})$$

has opposite parity for even and odd l, with respect to the coordinates 1, 2, $\cdots$, N. Therefore, (4.9) defines two sets of equations in which the even spherical waves are coupled and the odd spherical waves are coupled, but there is no mixing. If one restricts onself to s and p waves, then there is no coupling at all.

Because we are considering scattering from a neutral atom the radial function $u_{lL^{(T)}S^{(T)}}(r_{1})/r_{1}$ approaches the asymptotic form of the spherical Bessel function with an appropriate phase shift. Thus

$$\lim_{r_{1}\to\infty}u_{lL^{(T)}S^{(T)}}(r_{1})\to\sin[kr_{1}-\tfrac{1}{2}\pi l+\delta_{lL^{(T)}S^{(T)}}]. \qquad (4.10)$$

The total cross section is related to the phase shift by

$$\sigma=\frac{4\pi}{k^{2}}\left(\frac{1}{2(2L+1)(2S+1)}\right)\sum_{l}\sum_{L^{(T)}S^{(T)}}(2L^{(T)}+1)\times(2S^{(T)}+1)\sin^{2}\delta_{lL^{(T)}S^{(T)}}. \qquad (4.11)$$

The integration involved in the integrals of (4.9) can be performed in well-known ways. The resulting equations are one dimensional integro-differential equations for the function $u_{lL^{(T)}S^{(T)}}(r_{1})$. The integral nature of the equations arises from the exchange terms, i.e., the terms multiplied by $(N-1)$, in (4.9).

The direct polarization terms give a contribution of the form (in atomic units):

$$-\frac{1}{r^{4}}\sum_{nll'}\alpha_{nl\to l'}(r), \qquad (4.11\mathrm{a})$$

where

$$\alpha_{nl\to l'}(r)=\kappa_{nl\to l'}\left[\int_{0}^{r}r_{2}u_{nl\to l'}(r_{2})u_{nl}(r_{2})dr_{2}+r^{3}\int_{r}^{\infty}u_{nl\to l'}(r_{2})u_{nl}(r_{2})\frac{dr_{2}}{r_{2}{}^{2}}\right].$$

The constants $\kappa_{nl\to l'}$ are numbers which, in addition to l', depend on the number of electrons there are in the nl shell. For atoms with closed shells they have been worked out by Sternheimer.[5] In the limit $r\to\infty$ the quantity $\sum\alpha_{nl\to l'}(r)$ approaches the polarizability

---

[7] The multiplication and integration of the equation by this factor is not a mathematically reversible step. Thus when one has solved the resulting radial equation, one cannot assert that the total function containing this radial function is an exact solution of the Schrödinger equation, even if Φ were the exact eigenfunction of the reduced Hamiltonian, I am indebted to Dr. T. D. Schultz for pointing out this fact to me.

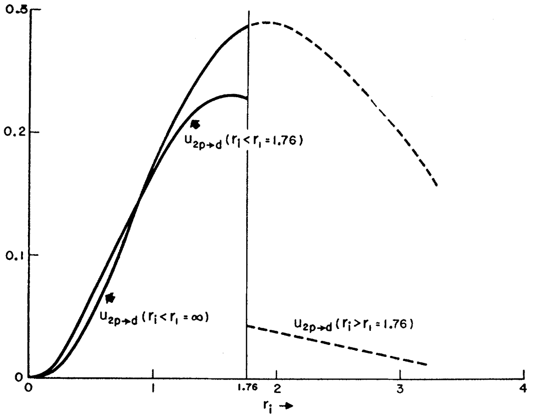

FIG. 1. Comparison of perturbed ($2p\to d$) neon functions for finite ($r_1=1.76$) and infinite values of r_1. Only the part to the left of the vertical line is used in the calculation.

α. The direct terms have the asymptotic form $-\alpha/r^4$, which is precisely the classical polarizability correction for large r. It is interesting that Bates and Massey,[8] working from the classical correction, introduced a term with the same asymptotic form into the wave mechanical Hamiltonian and found phase shifts as a function of the polarizability parameter α. The present method, therefore, can be considered a more rigorous justification of the semiphenomenological polarization correction of Bates and Massey. In the present method, however, the polarizability is no longer a parameter, but a definite number which comes naturally out of the formalism, and is Sternheimer's value in the approximation (3.14).

It should be noted, however, that there are exchange polarization terms included in the exchange terms of (4.9), so that the present method effectively goes beyond the polarizability correction of Bates and Massey. An example of such a term, after all other variables have integrated out, is

$$u_{2p\to d}(r_1)\left[\frac{1}{r_1^3}\int_0^{r_1} r_2^2 u_{2p}(r_2)u_{0S^{(T)}}(r_2)\frac{dr_2}{r_2^2}+r_1^2\int_{r_1}^{\infty} u_{2p}(r_2)u_{0S^{(T)}}(r_2)\frac{dr_2}{r_2^5}\right].$$

The second integral implies that the argument, r_2, of the unperturbed orbital is greater than the argument of the perturbed orbital $u_{2p\to d}(r_1)$. But the dipole approximation, which is reflected in the Eq. (3.19) for the perturbed orbital, implies $r_1>r_2$. This brings us to our final approximation, which can be stated in the following way. Any term which consists of a product of functions u_{nl} and $u_{nl\to l'}$, in which the argument of the perturbed orbital is implicitly less than that of the unperturbed orbital, is neglected. (This is not applied when the arguments are the same.) Physically this means, roughly, taking into account the polarization of only those parts of the atomic orbitals which are within the scattered particle. This approximation is consistent with the dipole approximation, as can be seen from the following argument. The dipole approximation assumes that the higher multipoles in the expansion of the interaction in (3.1) have a small effect on the scattering; however, from their mathematical form, they become almost as important in the region $r_1<r_i$ as the dipole term itself. Therefore, if the higher multipoles have a small effect, then the same must be the case for the inner part of the dipole term; and this is what the present approximation neglects.

There is another approximation which this method implicitly assumes, which is also related to the above considerations, and which needs further discussion. Had we extended the solution to the region $r_1<r_i$, then, because of the inverted roles of r_1 and r_i in the dipole approximation (3.1), the function would have satisfied a different differential equation from (3.19), the inhomogeneous term being replaced by $u_{nl}(r)/r^2$. The parameter λ in (3.22) would, by the same inversion, go go over into r_1. The form of $\lambda\Phi_i'$ in (3.22) would therefore be different. The boundary condition that $\lambda\Phi_i'$ be continuous at $r_1=r_i$ reduces to the condition

$$\left.\frac{u_{nl\to l'}(r_i<r_1)}{r_1^2}\right|_{r_1=r_i}=\left.r_1u_{nl\to l'}(r_i>r_1)\right|_{r_1=r_i}. \tag{4.12}$$

Thus the perturbed $u_{nl\to l'}(r_i)$ has a discontinuity at $r_1=r_i$. When one solves (3.19) over the whole range of $r(=r_i)$, one implicitly assumes $r_1=\infty$. Now the above approximation neglects the region $r_i>r_1$, but it also implicitly uses that portion of the function $u_{nl\to l'}(r_i)$ for $r_i<r_1$ computed on the basis that $r_1=\infty$. The approximation is necessary in order to make the function $u_{nl\to l'}(r_i)/r_1^2$ a separable one. The question is how much does this function differ from a function which is appropriately matched according to (4.12). Clearly as $r_1\to\infty$ the two functions approach each other. In the region $r_1\to 0$ the effect of the polarization terms vanishes so discrepancies are unimportant. The question then is: how do the functions compare in the intermediate range of r_1? In Fig. 1 we have plotted approximate ($2p\to d$) functions for neon, calculated for $r_1=\infty$ and as appropriately matched by (4.12) for the value $r_1=1.76$. According to our approximation, it is the function in the region $r_i<1.76$ alone which is used. One sees from the graph that the agreement is very good even at this comparatively small value of r_1. (In the application of Sec. V, r_1 ranged to 9.6.) The agreement will clearly improve as r_1 gets bigger, so that this implicit approximation also seems like a very good one.

One more point worth mentioning before we leave this general discussion is the fact that, because of the parametric dependence of $\Phi^{(\text{pol})}$ on the scattered par-

---

[8] D. R. Bates and H. S. W. Massey, Trans. Roy. Soc. (London) **A239**, 269 (1943).

ticle, the general method will yield terms which can legitimately be interpreted as dynamic effects of the motion of the charge cloud as induced by the incoming electron. However, because of the parity change of the perturbed orbitals which results from the dipole approximation, these dynamic effects can manifest themselves only in exchange terms.

V. APPLICATION TO THE S-WAVE SCATTERING FROM OXYGEN

We have retained only the $(2p\to d)$ orbitals in the application of the method to the s-wave scattering from atomic oxygen. In the present instance our object was to get a quantitative estimate of the relative importance of the exchange polarization terms as compared to the direct polarization terms. As a general procedure this approximation is not recommended as the most consistent one for utilizing the potentialities of the method. This will be discussed in the succeeding paragraphs.

The $(2p\to d)$ orbitals make a contribution of 3.6 a_0^3 to the polarizability. The experimental value is about 5.1 a_0^3,[9] so that this amounts to about 70% of the total. Sternheimer has shown that the contribution of $(nl\to l')$ and $(nl'\to l)$ orbitals tend to cancel for atoms and ions with closed shells. In oxygen, whose $2p$ shell is not filled, the cancellation is not as complete.

The ground state of oxygen is a ${}^3P$ state, hence an s wave can scatter in two states from it: $S^{(T)}=\frac{3}{2}$ (quartet), and $S^{(T)}=\frac{1}{2}$ (doublet). Below we have written the integro-differential equation in atomic units. We have abbreviated the function $u_{lL^{(T)}S^{(T)}}$ by $u_{0S^{(T)}}$.

$$
\begin{aligned}
&\frac{d^2}{dr_1^2}u_{0S^{(T)}}(r_1)+\frac{16}{r_1}u_{0S^{(T)}}(r_1)-4u_{0S^{(T)}}(r_1)\{y_0(1s,1s;1)+y_0(2s,2s;1)+2y_0(2p,2p;1)+k^2\}\\
&\quad+2u_{1s}(r_1)\Big\{y_0(1s,0S^{(T)};1)+7[R_0(1s,0S^{(T)},1s,1s)+2R_0(1s,0S^{(T)},2s,2s)+4R_0(1s,0S^{(T)},2p,2p)\\
&\quad-R_0(2s,0S^{(T)},1s,2s)]-\frac{1}{2}\int_0^\infty u_{1s}(r_2)\left[\frac{d^2}{dr_2^2}u_{0S^{(T)}}(r_2)+\frac{16}{r_2}u_{0S^{(T)}}(r_2)+k^2u_{0S^{(T)}}(r_2)\right]dr_2\\
&\quad-8A_1(S^{(T)})R_1(2p,0S^{(T)},1s,2p)\Big\}+2u_{2s}(r_1)\Big\{y_0(2s_0,0S^{(T)};1)+7[2R_0(2s,0S^{(T)},1s,1s)+R_0(2s,0S^{(T)},2s,2s)\\
&\quad+4R_0(2s,0S^{(T)},2p,2p)-R_0(1s,0S^{(T)},1s,2s)]-8A_1(S^{(T)})R_1(2p,0S^{(T)},1s,2p)\\
&\qquad\qquad\qquad\qquad-\frac{1}{2}\int_0^\infty u_{2s}(r_2)\left[\frac{d^2}{dr_2^2}+\frac{16}{r_2}+k^2\right]u_{0S^{(T)}}(r_2)dr_2\Big\}\\
&=-\frac{32}{9r_1^2}u_{0S^{(T)}}(r_1)y_1(2p,\ 2p\to d;1)+u_{1s}(r_1)\left[\frac{32}{9}R_1\left(1s,\frac{0S^{(T)}}{r_2^2},\ 2p,\ 2p\to d\right)+A_2(S^{(T)})\int_0^\infty dr_2u_{2p}(r_2)u_{0S^{(T)}}(r_2)\right.\\
&\quad\left.\times\int_{r_2}^\infty\frac{dr_3}{r_3^3}u_{1s}(r_3)u_{2p\to d}(r_3)\right]+u_{2s}(r_1)\left[\frac{32}{9}R_1\left(2s,\frac{0S^{(T)}}{r_2^2},\ 2p,\ 2p\to d\right)+A_2(S^{(T)})\int_0^\infty dr_2u_{2p}(r_2)u_{0S^{(T)}}(r_2)\right.\\
&\qquad\qquad\left.\times\int_{r_2}^\infty\frac{dr_3}{r_3^3}u_{2s}(r_3)u_{2p\to d}(r_3)\right]+A_2(S^{(T)})u_{2p\to d}(r_1)\frac{1}{r_1^3}\int_0^{r_1}u_{2p}(r_2)u_{2p\to d}(r_2)dr_2. \qquad (5.1)
\end{aligned}
$$

In this equation the notation has the following meaning: k^2= energy in Rydbergs = 13.6 ev,

$$
y_t(c,d;i)\equiv\frac{1}{r_i^{t+1}}\int_0^{r_i}u_c(r_2)u_d(r_2)r_2^t dr_2+r_i^t\int_{r_i}^\infty u_c(r_2)u_d(r_2)\frac{dr_2}{r_2^{t+1}}, \qquad (5.2)
$$

$$
R_t\left(a,\frac{b}{r_3^i},c,d\right)\equiv\int_0^\infty u_a(r_3)\left(\frac{u_b(r_3)}{r_3^i}\right)y_t(c,d;3)dr_3. \qquad (5.3)
$$

The parameters $A_i(S)$ are defined in the following table:

	$A_0(S^{(T)})$	$A_1(S^{(T)})$	$A_2(S^{(T)})$
$S^{(T)}=\frac{1}{2}$(doublet)	0	1/18	32/45
$S^{(T)}=\frac{3}{2}$(quartet)	$-\frac{1}{4}$	1/8	8/5

We have put the polarization terms on the right-hand side of (5.1). The term multiplied by $u_{0S^{(T)}}(r_1)$ is the direct polarization contribution $\alpha_{2p\to d}(r_1)/r_1^4$ of (4.11a). The remaining terms are exchange terms.

In Fig. 2 we have plotted the function $u_{2p\to d}(r)$ for

---

[9] D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. (London) **A192**, 1 (1947).

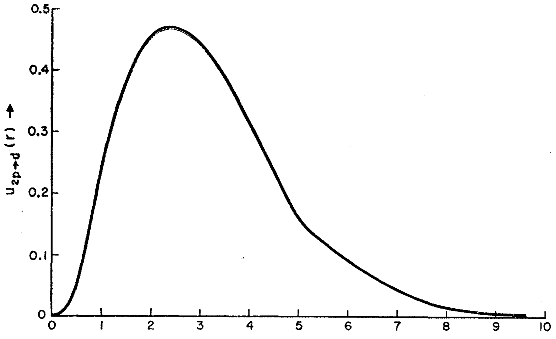

FIG. 2. $u_{2p\to d}(r)$ *versus* r (in atomic units) for atomic oxygen.

oxygen. In Fig. 3 the cross section *vs* energy is plotted in various approximations. Curve (*c*) corresponds to neglecting the right-hand side of (5.1) altogether. Curve (*a*) includes only the direct term, and curve (*b*) all terms. Curve (*d*) is a plot of Bates and Massey's results as taken from Seaton.[2] Their results are based on Buckingham's value of the polarizability.[10] All our equations were integrated numerically on the M.I.T. electronic computer Whirlwind I.

The most significant result is the effect of the exchange polarization terms. One can see that curve (*b*) differs from curve (*a*) by about 15%. This places an order of magnitude on the relative importance of these exchange terms. From an exact quantitative point of view, therefore, they are important, but from a less quantitative point of view the direct term seems to provide a good first approximation beyond the no-polarization approximation.

The relative importance of the direct ($2p\to s$) and ($2s\to p$) terms is probably overestimated by Bates' curve (*d*). The cross section is very sensitive to the polarizability and is close to its smallest value at $\alpha=5.7\ a_0^3$. At the experimental value of 5.1 a_0^3 their curve would be higher than (*d*), and the indications are that Sternheimer's value will be somewhat smaller than this; hence the cross-section curve for his value would be even higher. Nevertheless, the omission would be a serious one if one were interested in maximum accuracy. As it is, these results together with those of Bates and Massey, pretty well bracket the cross section between curves (*b*) and (*d*).

The effect of the exchange terms is much more unpredictable. Even in those atoms with closed shells the cancellation of the ($nl\to l'$) and ($nl'\to l$) orbitals only occurs in the direct terms. The exchange terms might very well add. It would seem, therefore, that for good accuracy one will have to include all ($nl\to l'$) orbitals for the largest occupied n shell. The perturbed orbitals coming from smaller n shells are small, corresponding to the tighter binding of these shells, so that they can reasonably be neglected.

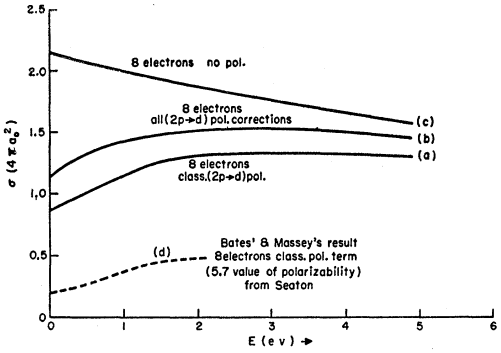

FIG. 3. Total s-wave cross section for oxygen *vs* energy in various approximations.

Coming back to oxygen, we can say that the present results definitely preclude any resonance in the s-wave scattering. However, the total cross section must include the effect of the p-wave. A rough calculation of Seaton[2] has shown that the p-wave cross section reaches approximately $4\pi a_0^2$ at an incident energy of 1.5 ev.

The over-all accuracy that the present method is capable of giving is difficult to estimate. Bates and Massey's classical polarizability correction differs from our direct terms for small values of r_1. Yet their results for $\alpha=3.6\ a_0^3$ at zero energy do not differ very much from our own, which seems to substantiate our assumption that polarization effects are minimized in the interior of the atom. The effect of neglecting the various self-consistent terms in deriving Sternheimer's equation is also uncertain. The relative insensitivity of the phase shift to exact form of the direct polarization correction indicates that, if the Sternheimer functions give a good value of the polarizability, they will give a good value of that part of the phase shift coming from the direct polarizability terms. The exchange terms are probably more sensitive to the form, but, as we have seen, they seem to have a smaller effect. If one is willing to solve the coupled equations (3.10) for the perturbed functions, one should get considerably better accuracy. By the same token the method is also applicable if one uses a cruder form of the perturbed orbitals (as gotten implicitly by Buckingham's method,[10] for example); however, with too crude a polarized orbital, it no longer becomes meaningul to include the exchange polarization terms.

ACKNOWLEDGMENTS

I wish to thank Professor Felix Villars and Professor Philip M. Morse for their constant help and encouragement throughout the development of this work. I am also indebted to Dr. Robert K. Nesbet and Mr. Leland Allen for valuable discussions on the subject of polarization. The correspondence of Dr. D. R. Bates, Dr. M. J. Seaton, and Dr. R. M. Sternheimer, plus helpful discussions with Dr. Seaton, is also acknowledged.

---

[10] R. A. Buckingham, Proc. Roy. Soc. (London) **A160**, 94 (1937).