may write

$$\langle\Omega\rangle_{Av}=[(\boldsymbol{\sigma}_{\frac{1}{2}}\cdot\boldsymbol{\sigma}_1)-3\zeta_{\frac{1}{2}}\zeta_1](\tfrac{3}{2}\langle\cos^2\vartheta\rangle_{Av}-\tfrac{1}{2}),$$

where ζ_i is the z-component of the operator $\boldsymbol{\sigma}_i$ in a coordinate system which has the symmetry axis as z-axis. Evidently for entirely free molecules in the state $J=0$, which is well known to be isotropic, $\langle\cos^2\vartheta\rangle_{Av}=\frac{1}{3}$ and hence

$$\langle\mathcal{H}'\rangle_{Av}=0.$$

Consequently no resonance for the free rotating HD molecule in its ground state can be expected and indeed none has been found experimentally[8] in solid HD, another proof that in solid hydrogen the molecules are rotating practically as freely as in the gaseous state.

Any anisotropy which may be produced by compression could, however, be traced by the appearance of a radio-frequency resonance. The spectrum would be given by the eigenvalues of

$$\langle\mathcal{H}'/h\rangle_{Av}=(\tfrac{3}{2}\langle\cos^2\vartheta\rangle_{Av}-\tfrac{1}{2})\times 43.7\Omega \text{ kc/sec},$$

where Ω has the eigenvalues -1, $\frac{1}{2}(1\pm\sqrt{3})$. The frequency observed measures directly the degree of deviation from random orientation, that is the deviation of $\langle\cos^2\vartheta\rangle_{Av}$ from the value $\frac{1}{3}$.

[8] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

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Theory of Ionization Probability Near Threshold*

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The behavior of the cross section for ionization by electron impact is investigated in the vicinity of threshold by means of the quantum theory of inelastic scattering. A Coulomb-modified form of the Born approximation is used to calculate the S-wave ionization cross sections for H^+, He^+, and He^{++}. The electron-nuclear interaction is included in the unperturbed Hamiltonian for the problem while the interaction between the incident and atomic electrons is considered as the perturbation. It can be shown that the limiting law for the ionization of a hydrogen atom has a linear dependence on the excess incident energy. The absolute cross sections evaluated are in good agreement with experiment. Generalization of the excess energy dependence of the threshold law to the case of multiple (n-fold) ionization is found to yield the forms E_{ex}^n for ionization by electron impact and E_{ex}^{n-1} for photoionization.

I. INTRODUCTION

In recent years the development of techniques for obtaining better ionization threshold curves[1–3] has aroused interest in the theoretical side of this problem. Most previous calculations[4,5] of ionization cross sections by electron impact have attempted to explain the gross features of the ionization probability curve over a very large electron energy range (~300 volts). In those cases the ordinary Born approximation was used to evaluate the direct ionization amplitude. The exchange amplitude was neglected since it is usually large only near the threshold.

Wannier[6] has derived a threshold law for single ionization which has the form of the 1.127th power of the excess energy. He obtained this via an approximate solution of the classical three-body problem coupled with certain statistical-mechanical arguments. A disadvantage of Wannier's result from an experimental point of view is that there is no way of knowing how far above the threshold this power law is supposed to be applicable. From a theoretical point of view, it appears more desirable to approach this problem within the conventional framework of the quantum theory of inelastic collisions so that all approximations made may be clearly delineated.

In the present calculation a modified form of the Born approximation is employed to obtain both the direct and exchange ionization (scattering) amplitudes. One *a priori* reason for expecting meaningful results from such a calculation is Wigner's[7] proof that the correct energy dependence of the cross section in the neighborhood of the threshold of a two-particle reaction is independent of the reaction mechanism but depends only on the long-range interaction of the product particles. In the concluding section we shall further discuss the justification for this procedure.

The method is here applied to the single ionization of hydrogen (atomic) and helium and to the double ionization of helium. Its formulation is described in detail for the hydrogen case. Its extension to helium follows in a parallel manner.

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[2] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. **84**, 859 (1951).
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[4] H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London) **140**, 613 (1933).
[5] B. Yavorsky, Compt. rend. acad. sci. U.R.S.S. **49**, 250 (1945).
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II. FORMULATION OF METHOD

The Schrödinger equation for two electrons (incident and bound) in the field of a fixed proton is

$$\{\nabla_1^2+\nabla_2^2-U(r_1)-U(r_2)+U(r_{12})+k^2\}\Psi(\mathbf{r}_1,\mathbf{r}_2)=0, \quad (1)$$

where $k^2=(2m/\hbar^2)$ times the total energy and $U(r)=(2m/\hbar^2)(-e^2/r)$. Expanding[8] the total wave function in terms of hydrogen atom eigenfunctions ψ_n,

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=e^{ikz_1}\psi_0(r_2)+\left(\sum_n+\int\right)F_n(\mathbf{r}_1)\psi_n(r_2), \quad (2a)$$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=\left(\sum_n+\int\right)G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1), \quad (2b)$$

multiplying by continuum wave function ψ_κ^* (which corresponds to ionization), and integrating over one of the position vectors gives the following two integro-differential equations (corresponding to direct and exchange ionization):

$$\{\nabla_1^2-U(r_1)+k^2-\kappa^2\}F_\kappa(\mathbf{r}_1)=-\int\psi_\kappa^*(\mathbf{r}_2)U(r_{12})\Psi(\mathbf{r}_1,\mathbf{r}_2)d\tau_2, \quad (3a)$$

$$\{\nabla_2^2-U(r_2)+k^2-\kappa^2\}G_\kappa(\mathbf{r}_2)=-\int\psi_\kappa^*(\mathbf{r}_1)U(r_{12})\Psi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1, \quad (3b)$$

where $\kappa^2=(2m/\hbar^2)$ times the energy of the ejected electron.

In the problem of excitation and in past treatments[4,5] of the ionization problem, the interaction potential appearing in the right of (3a, b) was taken as $U(r_{1\text{ or }2})-U(r_{12})$ and a plane wave operator appeared on the left. The use of an interaction potential which is asymmetrical in the two electrons has led in the past to the so-called "post-prior discrepancy"[9] in the case of exchange scattering. Several authors[10–13] have recently shown that the discrepancy vanishes when exact bound state wave functions are used but the situation is still unclear for the case of continuum states.[14] In the present case of ionization near threshold, the scattered electron as well as the ejected electron is under the influence of the Coulomb field of the ion core at all distances. Thus, the ion-electron interaction is regarded as part of the unperturbed Hamiltonian of the scattered electron by including this term on the left-hand side of (3). No "post-prior discrepancy" arises here since we have a symmetrical electron-electron interaction as the perturbation. This formulation of the problem was first applied to atomic scattering processes by Borowitz[12] in a calculation on the elastic scattering of electrons by hydrogen.

We expand the right-hand sides of (3a) and (3b) in spherical harmonics (suppressing the subscripts identifying the electrons):

$$-\int\psi_\kappa^*(\mathbf{r}')U(|\mathbf{r}-\mathbf{r}'|)\Psi(\mathbf{r},\mathbf{r}')d\tau'=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}A_l^m(r)P_l^m(\cos\theta)e^{im\varphi}, \quad (4a)$$

$$-\int\psi_\kappa^*(\mathbf{r}')U(|\mathbf{r}-\mathbf{r}'|)\Psi(\mathbf{r}',\mathbf{r})d\tau'=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}C_l^m(r)P_l^m(\cos\theta)e^{im\varphi}, \quad (4b)$$

where the polar axis is taken in the positive Z-direction, the direction of the incident beam. If we similarly expand $F_\kappa(\mathbf{r})$ and $G_\kappa(\mathbf{r})$,

$$F_\kappa(\mathbf{r})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}B_l^m(r)P_l^m(\cos\theta)e^{im\varphi}, \quad (5a)$$

$$G_\kappa(\mathbf{r})=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}D_l^m(r)P_l^m(\cos\theta)e^{im\varphi}, \quad (5b)$$

substitute these expansions into (3a) and (3b) and integrate over angle, the following radial equations result:

$$\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+k_q^2-U(r)-\frac{l(l+1)}{r^2}\right\}B_l^m=A_l^m, \quad (6a)$$

$$\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+k_q^2-U(r)-\frac{l(l+1)}{r^2}\right\}D_l^m=C_l^m, \quad (6b)$$

where $k_q^2=k^2-\kappa^2=(2m/\hbar^2)$ times the energy of the scattered electron. The Green's function solutions of these equations which vanish at the origin and are purely outgoing at infinity are

$$B_l^m=-k_qL_l\int_r^\infty H_lA_l^mr^2dr-k_qH_l\int_0^r L_lA_l^mr^2dr, \quad (7a)$$

$$D_l^m=-k_qL_l\int_r^\infty H_lC_l^mr^2dr-k_qH_l\int_0^r L_lC_l^mr^2dr, \quad (7b)$$

where L_l is the solution of the homogeneous equation in (6) which vanishes at the origin and H_l is the solution which is purely outgoing at infinity. The regular and

[8] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, New York, 1949), second edition, pp. 136, 140.

[9] Bates, Fundaminsky, and Massey, Trans. Roy. Soc. (London) **243**, 93 (1950).

[10] S. Borowitz and B. Friedman, Phys. Rev. **89**, 441 (1953).

[11] S. Altshuler, Phys. Rev. **91**, 1167 (1953).

[12] S. Borowitz, Phys. Rev. **96**, 1523 (1954).

[13] E. Corinaldesi and L. Trainor, Nuovo cimento **9**, 940 (1952).

[14] *Note added in proof.*—I am indebted to Dr. S. Borowitz for bringing to my attention the fact that the "post-prior discrepancy" also vanishes for continuum states when exact atomic wave functions are used. See A. Dalgarno, Phys. Rev. **91**, 198 (1953); S. Borowitz and B. Friedman, Phys. Rev. **93**, 251 (1954).

irregular solutions[15,16] of the Coulomb radial equation have the following asymptotic forms, respectively:

$$L_l \sim (k_q r)^{-1} \sin(k_q r - \alpha_q \ln 2k_q r - \tfrac{1}{2}l\pi + \eta_l),$$
$$K_l \sim (k_q r)^{-1} \cos(k_q r - \alpha_q \ln 2k_q r - \tfrac{1}{2}l\pi + \eta_l),$$

where $\alpha_q = -Zme^2/\hbar^2 k_q$, $\eta_l = \arg\Gamma(l+1+i\alpha_q)$, and Z is the charge of the ion core. The linear combination

$$H_l = K_l + iL_l \sim (k_q r)^{-1} \exp[i(k_q r - \alpha_q \ln 2k_q r - \tfrac{1}{2}l\pi + \eta_l)]$$

has the desired outgoing form at infinity. Upon substituting into (7), the asymptotic forms of the desired solutions to Eqs. (6a) and (6b) are

$$B_l{}^m \sim -r^{-1} \exp[i(k_q r - \alpha_q \ln 2k_q r - \tfrac{1}{2}l\pi + \eta_l)] \times \int_0^\infty L_l A_l{}^m r^2 dr, \quad (8a)$$

$$D_l{}^m \sim -r^{-1} \exp[i(k_q r - \alpha_q \ln 2k_q r - \tfrac{1}{2}l\pi + \eta_l)] \times \int_0^\infty L_l C_l{}^m r^2 dr. \quad (8b)$$

The direct and exchange ionization amplitudes are defined as the amplitudes at infinity of the outgoing scattered wave, that is,

$$F_\kappa(\mathbf{r}) \sim -r^{-1} \exp[i(k_q r - \alpha_q \ln 2k_q r)] f_\kappa(\theta,\varphi), \quad (9a)$$
$$G_\kappa(\mathbf{r}) \sim -r^{-1} \exp[i(k_q r - \alpha_q \ln 2k_q r)] g_\kappa(\theta,\varphi). \quad (9b)$$

Combining (5), (8), and (9), we have the following for the amplitudes:

$$f_\kappa(\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \exp[i(-\tfrac{1}{2}l\pi + \eta_l)] \times \left[\int_0^\infty L_l A_l{}^m r^2 dr\right] P_l{}^m(\cos\theta) e^{im\varphi}, \quad (10a)$$

$$g_\kappa(\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \exp[i(-\tfrac{1}{2}l\pi + \eta_l)] \times \left[\int_0^\infty L_l C_l{}^m r^2 dr\right] P_l{}^m(\cos\theta) e^{im\varphi}. \quad (10b)$$

The Born approximation is introduced by putting for the true solution, $\Psi(\mathbf{r},\mathbf{r}')$, in (4a) and (4b) the initial state, $e^{ik_p z}\psi_0(r')$. In order to avoid confusing the present method with the conventional Born approximation (asymmetrical perturbation and plane wave Green's function), we shall refer to it as the Coulomb-modified Born approximation. With this approximation, the evaluation of $A_l{}^m$ and $C_l{}^m$ still remains mathematically intractable. This difficulty may be overcome by decomposing the incident wave into its partial waves corresponding to different values of the orbital angular momentum. No great mathematical difficulties are encountered in the calculation of each partial cross section. In what follows, the calculations are carried through for the S partial cross section. Since we are interested only in the threshold behavior, it is certainly physically reasonable that the primary contribution to the total cross section will come from the S partial wave.

[15] See reference 8, pp. 52, 111.
[16] W. Gordon, Z. Physik **48**, 180 (1928).

III. HYDROGEN

The total ionization cross section for hydrogen is

$$\int_0^{\kappa_{\max}} d\kappa \int d\Omega \int d\omega \frac{k_q}{k_p} \{\tfrac{3}{4}|f_\kappa - g_\kappa|^2 + \tfrac{1}{4}|f_\kappa + g_\kappa|^2\}, \quad (11)$$

where the two angular integrations refer to the angles of the ejected and scattered electrons and the κ integration goes over all energies of the ejected electron consistent with energy conservation. The above combination of direct and exchange amplitudes is that required by the Pauli principle[17] for an incident beam of unpolarized electrons.

In the S-wave Born approximation the general spherical harmonic expansions of the preceding section may be specialized to the expansions in Legendre polynomials,

$$-\int \psi_\kappa^*(\mathbf{r}') U(|\mathbf{r}-\mathbf{r}'|) \frac{\sin k_p r}{k_p r} \psi_0(r') d\tau' = \sum_{l=0}^{\infty} A_l{}^{(0)}(r) P_l(\cos\theta), \quad (12a)$$

$$-\int \psi_\kappa^*(\mathbf{r}') U(|\mathbf{r}-\mathbf{r}'|) \frac{\sin k_p r'}{k_p r'} \psi_0(r) d\tau' = \sum_{l=0}^{\infty} C_l{}^{(0)}(r) P_l(\cos\theta), \quad (12b)$$

where the polar axis is now taken to be directed along $\boldsymbol{\kappa}$. The superscript in parentheses refers to the angular momentum of the incident partial wave. The amplitudes, when found by the method of Part II, are

$$f_\kappa{}^{(0)}(\theta) = \sum_{l=0}^{\infty} \exp[i(-\tfrac{1}{2}l\pi + \eta_l)] \times \left[\int_0^\infty L_l A_l{}^{(0)} r^2 dr\right] P_l(\cos\theta),$$

$$g_\kappa{}^{(0)}(\theta) = \sum_{l=0}^{\infty} \exp[i(-\tfrac{1}{2}l\pi + \eta_l)] \times \left[\int_0^\infty L_l C_l{}^{(0)} r^2 dr\right] P_l(\cos\theta).$$

[17] See reference 8, p. 143.

When the integration is performed over all angles, we have

$$\int d\Omega \int d\omega |f_\kappa^{(0)} \pm g_\kappa^{(0)}|^2 = 16\pi^2 \sum_{l=0}^{\infty} \frac{1}{2l+1} \left| \int_0^\infty L_l (A_l^{(0)} \pm C_l^{(0)}) r^2 dr \right|^2.$$

The properly normalized continuum functions for hydrogen were given by Sommerfeld[18] in an integral representation as

$$\psi_\kappa^*(\mathbf{r}) = \frac{\kappa}{2\pi} \left(\frac{\alpha}{e^{2\pi\alpha}-1} \right)^{\frac{1}{2}} \frac{e^{i\kappa r}}{\Gamma(1+i\alpha)} \int_0^\infty u^{i\alpha} e^{-u} \times J_0(2[i\kappa\xi u]^{\frac{1}{2}}) du,$$

where $\alpha = -Zme^2/\hbar^2\kappa$ and $\xi = r(1+\cos\theta)$. This can also be expressed as the expansion in Legendre polynomials,

$$\frac{\kappa}{2\pi} \left(\frac{\alpha}{e^{2\pi\alpha}-1} \right)^{\frac{1}{2}} \frac{e^{\frac{1}{2}\pi\alpha}}{\Gamma(1+i\alpha)} \sum_{l=0}^{\infty} (2l+1)(-i)^l \times e^{i\eta_l} L_l(\kappa,r) P_l(\cos\theta). \quad (13)$$

We now also expand the interaction potential in Legendre polynomials:

$$U(|\mathbf{r}-\mathbf{r}'|) = -\frac{2me^2}{\hbar^2} \sum_{n=0}^{\infty} P_n(\cos\gamma) h_n(r,r'), \quad (14)$$

where

$$h_n(r,r') = \begin{cases} r'^n/r^{n+1}, & r' < r \\ r^n/r'^{n+1}, & r' > r \end{cases}$$

and γ is the angle between the vectors $\mathbf{r}$ and $\mathbf{r}'$. The regular Coulomb function[19] which has the required asymptotic behavior is

$$L_l(k_q,r) = e^{-\frac{1}{2}\pi\alpha_q} \frac{|\Gamma(l+1+i\alpha_q)|}{(2l+1)!} (2k_q r)^l e^{ik_q r} \times {}_1F_1(i\alpha_q+l+1; 2l+2; -2ik_q r). \quad (15)$$

Using (12), (13), (14), and (15), one obtains

$$\int_0^\infty L_l(A_l^{(0)} \pm C_l^{(0)}) r^2 dr = 4\pi^{-\frac{1}{2}} a_0^{\frac{1}{2}} \beta_p^{-1} \left(\frac{\beta}{1-e^{-2\pi/\beta}} \right)^{\frac{1}{2}} \frac{e^{\pi/2\beta_q}}{\Gamma(1-i/\beta)} \frac{2^{2l}(-i)^l e^{i\eta_l}}{[(2l+1)!]^2} \times \beta^l \beta_q^l |\Gamma(l+1-i/\beta)| \cdot |\Gamma(l+1-i/\beta_q)| S_l^{\pm}(\beta,\beta_q), \quad (16)$$

where

$$S_l^{\pm} = \int_0^\infty \rho^{l+1} \sin\beta_p \rho \left[\Phi_l(\beta_q,\rho) \int_0^\infty \rho'^{l+2} e^{-\rho'} h_l(\rho,\rho') \times \Phi_l(\beta,\rho') d\rho' \pm \Phi_l(\beta,\rho) \int_0^\infty \rho'^{l+2} \times e^{-\rho'} h_l(\rho,\rho') \Phi_l(\beta_q,\rho') d\rho' \right] d\rho,$$

and

$$\Phi_l(\beta,\rho) = e^{i\beta\rho} \, {}_1F_1\left(-\frac{i}{\beta} + l + 1; 2l+2; 2i\beta\rho \right).$$

The new dimensionless variable ρ is related to r by $\kappa r = \beta\rho$ and $\beta = -1/\alpha$. While α and α_q are large and negative near threshold, β and β_q are small and positive.

To further reduce (16) we employ the low-energy expansion of the Coulomb function in powers of the energy which was first developed by Beckerley[20,21]:

$$\Phi_l(\beta,\rho) = \Lambda_{2l+1}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) - \frac{\beta^2\rho^2}{3(2l+2)} \left[\Lambda_{2l+2}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) + \frac{l}{2l+3} \Lambda_{2l+3}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) \right] + \frac{\beta^4\rho^4}{18(2l+2)(2l+3)} \times \left[\Lambda_{2l+3}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) + \frac{2}{5} \frac{5l-1}{2l+4} \Lambda_{2l+4}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) + \frac{l(5l+1)}{5(2l+4)(2l+5)} \Lambda_{2l+5}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) \right] - \cdots,$$

with

$$\Lambda_n(x) = \frac{n!}{(x/2)^n} J_n(x).$$

This expansion[22] is convergent for $\frac{1}{6}\rho^{\frac{3}{2}}\beta^2 \leqslant 1$ and, for the low energies involved, the important contribution to the integrals in $S_l^{\pm}$ come from well within the convergence radius of ρ. With the use of the low-energy expansion for Φ, $S_l^{\pm}$ may be written as

$$\frac{[(2l+1)!]^2}{2^{2l+1}} \left\{ (1 \pm 1) \mathfrak{A}_l - \frac{1}{3\sqrt{2}} (\beta^2 \pm \beta_q^2) \mathfrak{B}_l - \frac{1}{3\sqrt{2}} (\beta_q^2 \pm \beta^2) \mathfrak{C}_l + O(\beta^4, \beta_q^4) \right\}, \quad (17)$$

where $\mathfrak{A}_l$, $\mathfrak{B}_l$, and $\mathfrak{C}_l$ are coefficients which are independent of β and β_q but which do depend on the slowly varying incident energy parameter, β_p:

$$\mathfrak{A}_l = \int_0^\infty \rho^{\frac{1}{2}} \sin\beta_p \rho J_{2l+1}(2^{\frac{1}{2}}\rho^{\frac{1}{2}}) \times \left[\int_0^\infty \rho'^{\frac{1}{2}} e^{-\rho'} h_l(\rho,\rho') J_{2l+1}(2^{\frac{1}{2}}\rho'^{\frac{1}{2}}) d\rho' \right] d\rho,$$

[18] A. Sommerfeld, Ann. Physik **11**, 257 (1931).
[19] See reference 8, p. 53.
[20] J. G. Beckerley, Phys. Rev. **67**, 11 (1945).
[21] M. Abramowitz, J. Math. Phys. **33**, 111 (1954).
[22] J. G. Beckerley, Ph.D. thesis, Stanford University, 1944 (unpublished).

$$\mathfrak{B}_l=\int_0^\infty \rho^{\frac{1}{2}}\sin\beta_p\rho J_{2l+1}(2^{\frac{1}{2}}\rho^{\frac{1}{2}})\left[\int_0^\infty \rho'^{3}e^{-\rho'}h_l(\rho,\rho')\times\left\{J_{2l+2}(2^{\frac{1}{2}}\rho'^{\frac{1}{2}})+\frac{l}{(2\rho')^{\frac{1}{2}}}J_{2l+3}(2^{\frac{1}{2}}\rho'^{\frac{1}{2}})\right\}d\rho'\right]d\rho,$$

$$\mathfrak{C}_l=\int_0^\infty \rho^2\sin\beta_p\rho\left\{J_{2l+2}(2^{\frac{1}{2}}\rho^{\frac{1}{2}})+\frac{l}{(2\rho)^{\frac{1}{2}}}J_{2l+3}(2^{\frac{1}{2}}\rho^{\frac{1}{2}})\right\}\times\left[\int_0^\infty \rho'^{\frac{3}{2}}e^{-\rho'}h_l(\rho,\rho')J_{2l+1}(2^{\frac{1}{2}}\rho'^{\frac{1}{2}})d\rho'\right]d\rho.$$

Converting the κ integration into a β^2 integration, we obtain the following for the cross section:

$$\sigma^{(0)}=256\pi^2a_0^2\beta_p^{-3}\sum_{l=0}^{\infty}\frac{1}{2l+1}\frac{2^{4l}}{[(2l+1)!]^4}\int_0^{\beta_{\max}^2}d\beta^2(e^{-2\pi/\beta}-1)^{-1}(e^{-2\pi/\beta_q}-1)^{-1}\times\mathcal{P}_l(\beta^2,\beta_q^2)\{\tfrac{3}{4}|S_l^-|^2+\tfrac{1}{4}|S_l^+|^2\},\quad(18)$$

where $\mathcal{P}_l(\beta^2,\beta_q^2)$ represents the polynomial

$$[\{1+l^2\beta^2\}\{1+(l-1)^2\beta^2\}\cdots\{1+\beta^2\}]\times[\{1+l^2\beta_q^2\}\{1+(l-1)^2\beta_q^2\}\cdots\{1+\beta_q^2\}]$$

with $\mathcal{P}_0(\beta^2,\beta_q^2)=1$. Since β and β_q are positive and $\ll 1$, $(e^{-2\pi/\beta}-1)^{-1}(e^{-2\pi/\beta_q}-1)^{-1}\cong 1$ to a very good approximation. This leaves the integrand of (18) as a series of terms in ascending powers of β^2 and β_q^2. Using energy conservation, $\beta_{\max}^2=\beta^2+\beta_q^2$, and performing the simple integration over β^2, one obtains a series in powers of $\beta_{\max}^2$, or the energy above threshold. Retaining terms up to order $\beta_{\max}^4$, the S ionization cross section for hydrogen is

$$\sigma^{(0)}=64\pi^2a_0^2\beta_p^{-3}\sum_{l=0}^{\infty}\frac{1}{2l+1}\left[\beta_{\max}^2\mathfrak{A}_l^2+\beta_{\max}^4\left\{-\frac{1}{3\sqrt{2}}\mathfrak{A}_l(\mathfrak{B}_l+\mathfrak{C}_l)+\frac{l}{6}(l+1)(2l+1)\mathfrak{A}_l^2\right\}+O(\beta_{\max}^6)\right].\quad(19)$$

The coefficient $\frac{1}{6}l(l+1)(2l+1)$ is used to denote the sum of the squares of the first l integers.

IV. HELIUM

The (a) single or (b) double ionization of helium may be treated by the present method if we regard the process as excitation to a state having (a) one continuum electron ($Z=1$) and one bound hydrogenic electron ($Z=2$), or (b) two continuum electrons ($Z=2$). Excitation will take place from the singlet ground state of helium to singlet and triplet final states. Application of the Pauli principle[9,23] yields, for the differential cross section,

$$(k_q/k_p)\{\tfrac{1}{4}|f_\kappa-g_\kappa|^2+\tfrac{3}{4}|g_\kappa|^2\},\quad(20)$$

where the first term refers to the singlet-singlet transition and second term the singlet-triplet transition. The preservation of individual spins throughout the collision requires that the singlet-triplet transition be possible only through electron exchange.

Expanding the total wave function in terms of helium atom eigenfunctions

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=e^{ik_pz_1}\psi_0(\mathbf{r}_2,\mathbf{r}_3)+\left(\sum_n+\int\right)F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2,\mathbf{r}_3),\quad(21a)$$

$$\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\left(\sum_n+\int\right)G_n(\mathbf{r}_3)\psi_n(\mathbf{r}_2,\mathbf{r}_1),\quad(21b)$$

the three-electron Schrödinger equation may be put in the following form:

$$\left(\sum_n+\int\right)\{\nabla_1^2+k^2-k_n^2-2U(r_1)+U(r_{12})+U(r_{13})\}\times\psi_n(\mathbf{r}_2,\mathbf{r}_3)[F_n(\mathbf{r}_1)+\delta_{n0}e^{ik_pz_1}]=0,\quad(22a)$$

$$\left(\sum_n+\int\right)\{\nabla_3^2+k^2-k_n^2-2U(r_3)+U(r_{13})+U(r_{23})\}\times\psi_n(\mathbf{r}_2,\mathbf{r}_1)G_n(\mathbf{r}_3)=0.\quad(22b)$$

At this point we begin to proceed in different ways for the cases of single and double ionization.

A. Single Ionization

We represent the final state of the helium atom by the approximate product function, $v_0(r_2)u_\kappa(\mathbf{r}_3)$, where u_κ is a hydrogenic continuum function for $Z=1$ (identical to the ψ_κ used for hydrogen) and v_0 is the hydrogenic ground state function for $Z=2$. This permits one to write the integro-differential equations for the scattered waves as

$$\left\{\nabla_1^2+k_q^2-2U(r_1)+\int U(r_{12})v_0^2(r_2)d\tau_2\right\}F_\kappa(\mathbf{r}_1)=-\int U(r_{13})\psi_\kappa^*(\mathbf{r}_2,\mathbf{r}_3)\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\tau_2d\tau_3,\quad(23a)$$

$$\left\{\nabla_3^2+k_q^2-2U(r_3)+\int U(r_{23})v_0^2(r_2)d\tau_2\right\}G_\kappa(\mathbf{r}_3)=-\int U(r_{13})\psi_\kappa^*(\mathbf{r}_2,\mathbf{r}_1)\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\tau_1d\tau_2.\quad(23b)$$

For all values of r except the region very close to the nucleus, the ion core will appear as a point charge to the outgoing electrons. This is equivalent to the approximation in the left-and sides of (23a, b) that

[23] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), first edition, p. 237.

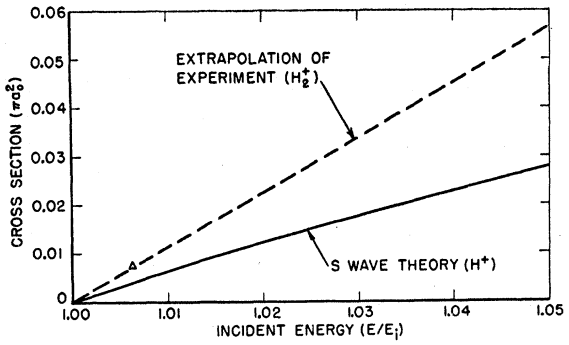

FIG. 1. Comparison of the calculated S-wave cross section with a linear extrapolation of the experimental curve for the ionization of hydrogen.

$-2U(r)+\int U(|\mathbf{r}-\mathbf{r}'|)v_0^2(r')d\tau'\cong -U(r)$. The right-hand sides of (23a, b) reduce to exactly the same quantities which enter for hydrogen, (12a, b), when we put for $\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ the approximate initial state function $(\sin k_p r_1/k_p r_1)v_0(r_2)u_0(r_3)$.

Since Eqs. (23a) and (23b) become identical to the corresponding equations for hydrogen, the principal difference in the ionization cross sections for the two atoms is expected to be due to the effect of the Pauli principle in prescribing how the amplitudes are to be combined, i.e., whether by (11) or by (20). The expression for the cross section in (18) is directly applicable to helium if the last bracket is replaced by $\frac{1}{4}|S_l^-|+\frac{3}{4}|\frac{1}{2}(S_l^+-S_l^-)|^2$. The final result for the cross section surprisingly comes out to be identical to (19) with the exception of an additional factor of $\frac{3}{4}$. This fortuitous situation exists because (1) $|f_\kappa^{(0)}-g_\kappa^{(0)}|^2$ does not contribute at all to terms up to order $\beta_{\max}{}^4$ in the cross section, and (2) the coefficients of $\beta_{\max}{}^2$ and $\beta_{\max}{}^4$ introduced by $|g_\kappa^{(0)}|^2$ are equal to those introduced by $|f_\kappa^{(0)}+g_\kappa^{(0)}|^2$ to within a constant factor. The coefficients of $\beta_{\max}{}^6$ and higher powers of the excess energy will be different for helium and hydrogen.

B. Double Ionization

The equations appropriate to the double ionization of helium,

$$\{\nabla_1^2+k_q^2-2U(r_1)\}F_\kappa(\mathbf{r}_1)=-\int[U(r_{12})+U(r_{13})]\psi_\kappa^*(\mathbf{r}_2,\mathbf{r}_3)\times\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\tau_2 d\tau_3, \quad (24a)$$

$$\{\nabla_3^2+k_q^2-2U(r_3)\}G_\kappa(\mathbf{r}_3)=-\int[U(r_{23})+U(r_{13})]\times\psi_\kappa^*(\mathbf{r}_2,\mathbf{r}_1)\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\tau_1 d\tau_2, \quad (24b)$$

are obtained from a simple rearrangement of (22a) and (22b). We use the same approximation for Ψ here as in Sec. A and the final state is taken as $v_\kappa(\mathbf{r}_2)v_{\kappa'}(\mathbf{r}_3)\delta(\kappa/\kappa+\kappa'/\kappa')$. The delta function is used symbolically to require the two ejected electrons to take asymptotic directions just opposite to each other as a result of their mutual repulsion. The right-hand sides of Eqs. (24a) and (24b) then become

$$-\delta\left(\frac{\kappa}{\kappa}+\frac{\kappa'}{\kappa'}\right)\frac{\sin k_p r_1}{k_p r_1}\left[\int v_{\kappa'}{}^*(\mathbf{r}_3)u_0(r_3)d\tau_3\right]\times\int U(r_{12})v_\kappa{}^*(\mathbf{r}_2)v_0(r_2)d\tau_2, \quad (25a)$$

$$-\delta\left(\frac{\kappa}{\kappa}+\frac{\kappa'}{\kappa'}\right)u_0(r_3)\left[\int v_{\kappa'}(\mathbf{r}_1)\frac{\sin k_p r_1}{k_p r_1}d\tau_1\right]\times\int U(r_{23})v_\kappa{}^*(\mathbf{r}_2)v_0(r_2)d\tau_2. \quad (25b)$$

When the direct and exchange amplitudes are found and combined according to (20), the integration over the direction of ejection of the two electrons gives only 4π because of the correlation represented by the delta function.

By means of a procedure very simllar to that found in Part III, we arrive at the following expression for the cross section:

$$\sigma^{(0)}=4\pi a_0{}^2\beta_p{}^{-3}\sum_{l=0}^{\infty}\frac{1}{2l+1}\cdot\frac{2^{4l}}{[(2l+1)!]^4}\times\int_0^{\beta_{\max}{}^2}\int_0^{\beta'{}_{\max}{}^2}(e^{-2\pi/\beta}-1)^{-1}(e^{-2\pi/\beta_q}-1)^{-1}\mathcal{P}_l(\beta^2,\beta_q{}^2)\times\{\tfrac{1}{4}|y_f T_l{}^f-y_g T_l{}^g|^2+\tfrac{3}{4}|y_g T_l{}^g|^2\}d\beta'^2 d\beta^2, \quad (26)$$

which, after making the low-energy expansion and

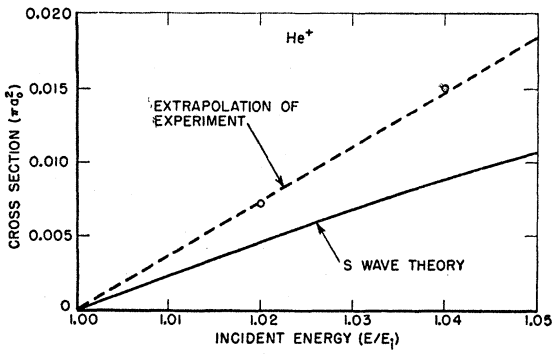

FIG. 2. Comparison of the calculated S-wave cross section with a linear extrapolation of the experimental curve for the single ionization of helium.

integrating over the allowed energies of the two ejected electrons, yields

$$\sigma^{(0)}=\frac{\pi}{2}a_0^2\beta_p^{-3}\sum_{l=0}^{\infty}\frac{1}{2l+1}[\beta_{\max}{}^4X_l$$

$$+\beta_{\max}{}^6\{Y_l+\tfrac{1}{9}l(l+1)(2l+1)X_l\}+O(\beta_{\max}{}^8)]. \quad (27)$$

The definitions of the quantities introduced in (26) and (27) are listed in Appendix I. It must be remembered that β^2 is the energy in units of one Rydberg for the cases of single ionization while it is the energy in units of four Rydbergs for the case of double ionization.

V. RESULTS AND DISCUSSION

The $\mathfrak{A}$'s, $\mathfrak{B}$'s, and $\mathfrak{C}$'s are evaluated by numerical integration in the region $\rho=0$ to 10. The integration from 10 to ∞ is performed by semianalytic means. The sums over l turn out to converge sufficiently rapidly to make necessary the inclusion of only the $l=0$, 1, and 2 terms. The S-wave cross sections are evaluated for an energy range above threshold equal to 5% of the ionization potential. This amounts to 0.68, 1.23, and 3.95 electron volts for H^+, He^+, and He^{++}, respectively. The resulting curves appear in Figs. 1, 2, and 3.

Absolute cross sections have been measured for the production of H_2^+ by Tate and Smith,[24] for He^+ by Smith,[25] and for He^{++} by Bleakney and Smith.[26] These experimental curves are reproduced in Fig. 4 from their original sources. The observed ionization probability for He^{++} has a small background of H_2^+ near threshold which we have subtracted out with the use of the ionization probability curve[24] for H_2^+. In Fig. 5 a plot of the square root of the He^{++} ionization curve shows that the cross section tends to go quadratically with the excess energy as threshold is approached. For the purpose of comparison with our calculated cross sections,

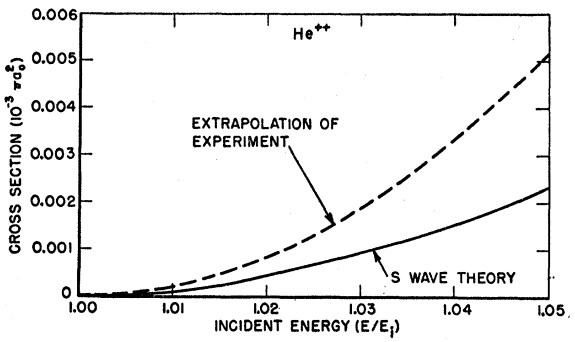

FIG. 3. Comparison of the calculated S-wave cross section with a quadratic extrapolation of the experimental curve for the double ionization of helium.

[24] J. T. Tate and P. T. Smith, Phys. Rev. 39, 270 (1932).
[25] P. T. Smith, Phys. Rev. 36, 1293 (1930).
[26] W. Bleakney and L. G. Smith, Phys. Rev. 49, 402 (1936).

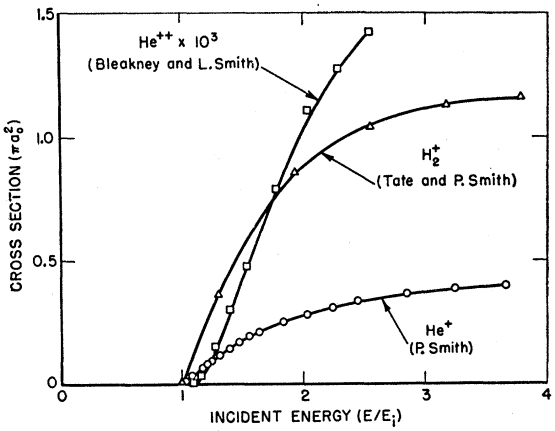

FIG. 4. Reproduction of experimental data on the absolute cross section for the single ionization of H_2 and He and the double ionization of He by electron impact.

the experimental curves are extrapolated to the threshold, linearly for H_2^+ and He^+ and quadratically for He^{++}.

The agreement between experiment and theory is surprisingly good. It can be shown that all higher partial cross sections have the same limiting dependence on the excess energy as does the S cross section. This is so because the Coulomb interaction will predominate over the centrifugal barrier at large distances for all values of the angular momentum. Hence, the higher partial cross sections will contribute to filling in the gap between experiment and the S partial cross section. For hydrogen we use the exact initial and final atomic wave functions so that our only source of error is the use of an approximate $\Psi(\mathbf{r},\mathbf{r}')$. If we guess that the cross section for ionization of H_2 is about 1.5 times that for ionization of H, this would leave an error of the order of 10% that may be attributable to use of the Coulomb-modified Born approximation. An experimental determination of the absolute cross section for ionization of hydrogen atoms near threshold, a difficult project, would be very useful in this connection. The contribution of the P partial wave is presently being investigated. In the calculation of the S cross sections for helium, we had to assume reasonable initial and final atomic wave functions. The agreement with experiment in these cases indicates that the assumed functions are not too bad.

The error introduced in (4a) and (4b) comes about because $e^{ik_pz}\psi_0(r')$ differs appreciably from the true Ψ for small values of r, that is, in the so-called reaction zone. We may visualize the radius of the reaction zone as varying inversely with the energy of the incident electron. This leads to a vanishingly small reaction zone in the high-energy limit, accounting for the applicability of the Born approximation there. In the present case involving energies near ionization threshold, the reaction zone radius is finite and of the order of a_0. However, the

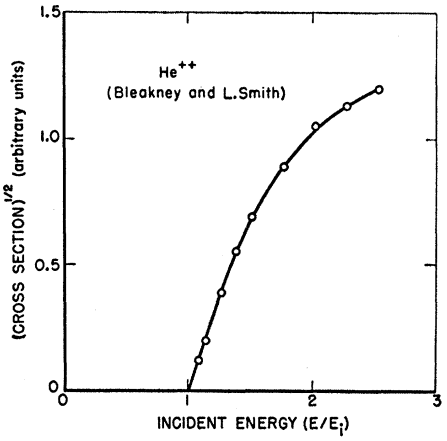

FIG. 5. Plot of the square root of the experimental cross section for the double ionization of He.

contribution to the integral in (4) which arises from the reaction zone will be relatively small since the continuum function ψ_κ^* is spread out over all space. In contrast, an excited state function which falls off exponentially will lead to a larger relative contribution to the integral from the reaction zone. Hence, our approximation might be expected to be less severe for the case of ionization than for elastic scattering or excitation.

There are very few experimental points lying in the small region near threshold in which the calculations are applicable. As a result we do not have adequate experimental verification of the exact shape of the ionization probability curve in this region. The experimental situation here is very difficult because the thermal spread of electron energies obscures the ionization probability variation which is sought. Recent results of Hickam, Fox, and Kjeldaas[27] show a linear ionization probability for He^+ down to about 0.2 ev above threshold. On the other hand, they also obtain a linear ionization probability curve for Xe^{++}, which is very hard to understand. Clarke[3] finds a quadratic initial curve for Xe^{++}, which agrees with the findings of this paper. Clearly, additional experimental work on the limiting shapes of ionization probability curves would be most helpful.

One may question whether the presently derived result of a limiting linear threshold law for the ionization of the hydrogen atom follows only as a consequence of using a form of the Born approximation, or whether this is a general law. The answer to this is that it is indeed a general limiting law and that the use of the exact value of $\Psi(\mathbf{r},\mathbf{r}')$ in (12a) and (12b) would merely result in the alteration of the $\mathfrak{A}$, $\mathfrak{B}$, and $\mathfrak{C}$ coefficients in the final expression for the cross section but would not affect the $\beta_{\max}^2$ dependence. The $\beta_{\max}^2$ dependence comes about entirely from the expansions of $L_l(k_q,r$e and $L_l(\kappa,r)$ for small values of k_q and κ. The total wav) function Ψ will depend on only k_p as a parameter; hence, its variation will be smooth through the ionization limit. The explicit steps in separating the κ dependence from the k_p dependence are given in Appendix II.

There is one additional generalization that may be made in treating the case of multiple ionization. If we represent the outgoing part of the final state of an n-ionized atom by a product of n continuum wave functions, the cross section near threshold will be of the form

$$\int_0^{\beta_{\max}^2} d\beta_n^2 \int_0^{\beta_{\max}^2-\beta_n^2} d\beta_{n-1}^2 \cdots \int_0^{\beta_{\max}^2-\beta_n^2-\cdots-\beta_2^2} d\beta_1^2$$

$$\times\{A(\beta_p)+\beta_q^2 B_q(\beta_p)+\sum_{i=1}^{n}\beta_i^2 B_i(\beta_p)+O(\beta_q^4,\beta_i^4)\}.$$

If we carry out this integration making use of energy conservation, we obtain a power series in $\beta_{\max}^2$ with a lead term proportional to $\beta_{\max}^{2n}$. In other words, the limiting law for n-fold ionization by electron impact is the nth power of the excess energy. The experimental verification of this is difficult[27,28] in many-electron atoms owing to the onset of alternate modes of ionization very close to the threshold. The most clear-cut experiment to verify an E_{ex}^n power law would be on an n-electron atom. We have seen this for He^{++} in Fig. 5. A feasible future experiment would perhaps be the measurement of the threshold behavior for Li^{+++} which has its onset at about 200 volts.

The process of photoionization leads to the case of only one electron moving away from an oppositely charged ion core. This situation corresponds to $n=0$ above because there are no integrations over β^2; the energy of the ejected electron is uniquely determined by the amount by which $h\nu$ exceeds the ionization energy. This leads to the appearance of a finite cross section at threshold as is commonly observed in photoionization measurements. It should be noted that the process of photoionization (single) is an example of the two-particle reaction discussed by Wigner[7] in which the reaction products have a Coulomb attraction between them. The generalization of our present results to the case of n-fold ionization by photon impact would yield a threshold curve varying as the $(n-1)$th power of the excess energy. We have not been able to find any experiments in the literature which measure cross sections for multiple photoionization.

ACKNOWLEDGMENTS

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[27] Hickam, Fox, and Kjeldaas, Phys. Rev. **96**, 63 (1954).

[28] W. Bleakney, Phys. Rev. **36**, 1303 (1930).

APPENDIX I

$$y_f=\int_0^\infty \rho^2 e^{-\rho/2}\Phi_0(\beta',\rho)d\rho=a_f-\beta'^2 b_f+\cdots,$$

$$y_g=\int_0^\infty \rho\sin\beta_p\rho\Phi_0(\beta',\rho)d\rho=a_g-\beta'^2 b_g+\cdots,$$

$$T_l{}^f=\int_0^\infty \rho^{l+1}\sin\beta_p\rho\Phi_l(\beta_q,\rho)\times\left[\int_0^\infty \rho'^{l+2}h_l(\rho,\rho')e^{-\rho'}\Phi_l(\beta,\rho')d\rho'\right]d\rho$$

$$=\frac{[(2l+1)!]^2}{2^{2l+1}}\left[\mathfrak{A}_l{}^f-\frac{1}{3\sqrt{2}}\beta^2\mathfrak{B}_l{}^f-\frac{1}{3\sqrt{2}}\beta_q{}^2\mathfrak{C}_l{}^f+\cdots\right],$$

$$T_l{}^g=\int_0^\infty \rho^{l+2}e^{-\rho/2}\Phi_l(\beta_q,\rho)\times\left[\int_0^\infty \rho'^{l+2}h_l(\rho,\rho')e^{-\rho'}\Phi_l(\beta,\rho')d\rho'\right]d\rho$$

$$=\frac{[(2l+1)!]^2}{2^{2l+1}}\left[\mathfrak{A}_l{}^g-\frac{1}{3\sqrt{2}}\beta^2\mathfrak{B}_l{}^g-\frac{1}{3\sqrt{2}}\beta_q{}^2\mathfrak{C}_l{}^g+\cdots\right],$$

$$a_f=\frac{1}{\sqrt{2}}\int_0^\infty \rho^{\frac{3}{2}}e^{-\rho/2}J_1(2^{\frac{3}{2}}\rho^{\frac{1}{2}})d\rho,$$

$$a_g=\frac{1}{\sqrt{2}}\int_0^\infty \rho^{\frac{1}{2}}\sin\beta_p\rho J_1(2^{\frac{3}{2}}\rho^{\frac{1}{2}})d\rho,$$

$$b_f=\frac{1}{6}\int_0^\infty \rho^3 e^{-\rho/2}J_2(2^{\frac{3}{2}}\rho^{\frac{1}{2}})d\rho,$$

$$b_g=\frac{1}{6}\int_0^\infty \rho^2\sin\beta_p\rho J_2(2^{\frac{3}{2}}\rho^{\frac{1}{2}})d\rho.$$

The $\mathfrak{A}_l{}^f$, $\mathfrak{B}_l{}^f$, and $\mathfrak{C}_l{}^f$ are identical to the $\mathfrak{A}_l$, $\mathfrak{B}_l$, and $\mathfrak{C}_l$ of Part III.

$$\mathfrak{A}_l{}^g=\int_0^\infty \rho^{\frac{3}{2}}e^{-\rho/2}J_{2l+1}(2^{\frac{3}{2}}\rho^{\frac{1}{2}})\times\left[\int_0^\infty \rho'^{\frac{3}{2}}e^{-\rho'}h_l(\rho,\rho')J_{2l+1}(2^{\frac{3}{2}}\rho'^{\frac{1}{2}})d\rho'\right]d\rho,$$

$$\mathfrak{B}_l{}^g=\int_0^\infty \rho^{\frac{3}{2}}e^{-\rho/2}J_{2l+1}(2^{\frac{3}{2}}\rho^{\frac{1}{2}})\times\left[\int_0^\infty \rho'^{3}e^{-\rho'}h_l(\rho,\rho')\left\{J_{2l+2}(2^{\frac{3}{2}}\rho'^{\frac{1}{2}})+\frac{l}{(2\rho')^{\frac{1}{2}}}J_{2l+3}(2^{\frac{3}{2}}\rho'^{\frac{1}{2}})\right\}d\rho'\right]d\rho,$$

$$\mathfrak{C}_l{}^g=\int_0^\infty \rho^3 e^{-\rho/2}\left\{J_{2l+2}(2^{\frac{3}{2}}\rho^{\frac{1}{2}})+\frac{l}{(2\rho)^{\frac{1}{2}}}J_{2l+3}(2^{\frac{3}{2}}\rho^{\frac{1}{2}})\right\}\times\left[\int_0^\infty \rho'^{\frac{3}{2}}e^{-\rho'}h_l(\rho,\rho')J_{2l+1}(2^{\frac{3}{2}}\rho'^{\frac{1}{2}})d\rho'\right]d\rho,$$

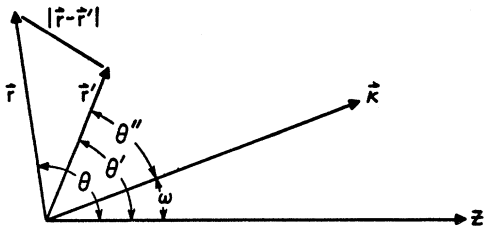

FIG. 6. Coordinate system for Appendix II.

$$X_l=a_f{}^2(\mathfrak{A}_l{}^f)^2-2a_f a_g\mathfrak{A}_l{}^f\mathfrak{A}_l{}^g+4a_g{}^2(\mathfrak{A}_l{}^g)^2,$$

$$Y_l=\frac{2}{3}\Big\{-a_f b_f(\mathfrak{A}_l{}^f)^2-4a_g b_g(\mathfrak{A}_l{}^g)^2+\mathfrak{A}_l{}^f\mathfrak{A}_l{}^g(a_f b_g+a_g b_f)-\frac{1}{3\sqrt{2}}\Big[a_f{}^2\mathfrak{A}_l{}^f(\mathfrak{B}_l{}^f+\mathfrak{C}_l{}^f)+4a_g{}^2\mathfrak{A}_l{}^g(\mathfrak{B}_l{}^g+\mathfrak{C}_l{}^g)-a_f a_g\{\mathfrak{A}_l{}^g(\mathfrak{B}_l{}^f+\mathfrak{C}_l{}^f)+\mathfrak{A}_l{}^f(\mathfrak{B}_l{}^g+\mathfrak{C}_l{}^g)\}\Big]\Big\}.$$

APPENDIX II

For small κ, the integral in Eq. (4a) may be written as

$$\sum_{l=0}^\infty \Theta_l(\kappa)\int r'^l[\Gamma_l(r')-\kappa^2\Delta_l(r')+\cdots]P_l(\cos\theta'')\times U(|\mathbf{r}-\mathbf{r}'|)\Psi(\mathbf{r},\mathbf{r}')d\tau'.$$

Using the addition theorem for Legendre polynomials on $P_l(\cos\theta'')$, multiplying by $P_\lambda{}^\mu(\cos\theta)e^{-i\mu\varphi}\sin\theta d\theta d\varphi$, and integrating over the angular part of $\mathbf{r}$ leads to the following φ,φ' integration:

$$(2-\delta_{m0})\int_0^{2\pi}\int_0^{2\pi} e^{-i\mu\varphi}\cos m\varphi' U(|\mathbf{r}-\mathbf{r}'|)\Psi(\mathbf{r},\mathbf{r}')d\varphi d\varphi'.$$

We carry out this integration by rotating the triangle having the sides $\mathbf{r}$, $\mathbf{r}'$, and $|\mathbf{r}-\mathbf{r}'|$ about the Z axis. (See Fig. 6.) In this operation $U\Psi$ will remain unchanged, giving for the integral $4\pi^2\delta_{\mu 0}\delta_{m0}U\Psi$. Thus the only property of Ψ we have invoked is its azimuthal symmetry about the Z axis. The resulting expression for the radially dependent coefficient in (4a) is

$$A_\lambda{}^\mu(r)=\pi(2\lambda+1)\frac{(\lambda-\mu)!}{(\lambda+\mu)!}\sum_{l=0}^\infty \Theta_l(\kappa)P_l(\cos\omega)\times\int_0^\infty dr'r'^{l+2}[\Gamma_l(r')-\kappa^2\Delta_l(r')+\cdots]\times\int_0^\pi\int_0^\pi \sin\theta d\theta\sin\theta' d\theta' P_\lambda(\cos\theta)\times P_l(\cos\theta')U(|\mathbf{r}-\mathbf{r}'|)\Psi(\mathbf{r},\mathbf{r}').$$

The limiting κ dependence here is independent of the functional form of Ψ.