Reexamination of Scattering by a Pair of Fixed Dipolar Charges*

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Upon careful examination of charged-particle scattering by a finite stationary dipolar system, it is found that the long-range nature of the dipole potential leads to divergence of the total scattering cross section. Thus, contrary to the results of Takanagi and Itikawa, the total cross sections for the finite dipole diverge in a manner similar to that found earlier by Mittleman and von Holdt for the point dipolar field.

I. INTRODUCTION

In order to better understand the scattering of electrons by polar molecules, a number of studies have been made of scattering by a simple dipolar system. Altshuler[1] determined the cross sections for electron scattering by a point dipole in the Born approximation. Later Mittleman and von Holdt[2] obtained an exact solution to the same problem. In both cases the total cross section diverges and in the latter case the momentum-transfer cross section also diverges for dipole moments greater than the critical value $D = 0.639ea_0$. The difficulties associated with the strong singularity in the potential function for a point dipole have been avoided by Shimizu,[3] who obtained the scattering amplitude and momentum-transfer cross sections for scattering by a finite dipole composed of two opposite charges fixed at a separation $R > 0$. The analysis of Shimizu[3] was later used in numerical calculations by Takayanagi and Itikawa,[4] who obtained both momentum-transfer and total scattering cross sections for low-energy electrons on a finite fixed dipole.

Now it is well known that scattering by a spherically symmetric potential with an r^{-2} asymptotic form leads to an infinite total scattering cross section.[5] The general behavior of the total cross section is not due to the strong singularity at the origin, but rather to the long-range nature of the interaction. The inverse square potential yields a very slow convergence of the phase shifts with the result that the series of partial cross sections does not converge and no total cross section exists.[5] Of course, the dipolar field is not spherically symmetric, but it does have a long range r^{-2} form. The dipole field is considerably more complicated because of the $\cos\theta$ dependence, where θ is the angle between the electron and the dipole axis. Nevertheless, Mittleman and von Holdt's[2] exact treatment of scattering by a pure dipole field led again to a divergent total cross section. It seems very reasonable that this divergence is also due to the long-range nature of the dipole field and not a result of the strong singularity at $r = 0$. However, since the results of Takayanagi and Itikawa[4] yielded a finite total cross section for the case of a finite stationary dipole, where no singularity exists, their results would indicate that the removal of the singularity at $r = 0$ also removes the divergence in the total cross section. We show that this is not the case. Instead, the total cross section does diverge and the finite results of Ref. 4 are due to numerical approximation in a nonconvergent series.

II. SCATTERING BY FINITE STATIONARY DIPOLE

It is easy to show from the analysis of Mittleman and von Holdt[2] that a modified dipolar potential, in which the singularity at the origin is removed, still leads to the same divergent behavior of the total cross section. This can be done most conveniently by imposing an infinitely repulsive core at $r = r_0$ in which case the scattering problem is described by the equations

$$(\nabla^2 + k^2 + \vec{\alpha}\cdot\vec{r}/r^3)\Psi(\vec{r}) = 0 , \quad r > r_0 \tag{1}$$

$$\Psi(\vec{r}) = 0 , \quad r < r_0 . \tag{2}$$

Here $k^2 = 2mE/\hbar$,

$$\vec{\alpha} = 2me\vec{\mathfrak{D}}/\hbar^2 , \tag{3}$$

and $\vec{\mathfrak{D}}$ is the dipole moment. Equation (1) is separable in spherical coordinates r, μ, φ, $(\mu = \cos\theta)$. A substitution of the form $\Psi(\vec{r}) = R(r)\Theta(\mu)e^{im\varphi}$ yields the separated equations

$$\left(\frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu} - \frac{m^2}{1-\mu^2} + \alpha\mu + L_n^m(L_n^m+1)\right)\Theta_n^m(\mu) = 0 , \tag{4}$$

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + k^2 - \frac{L_n^m(L_n^m+1)}{r^2}\right)R_n(r) = 0 . \tag{5}$$

The eigenfunctions $\Theta_n^m(\mu)$ and eigenvalues $L_n^m(L_n^m+1)$ of Eq. (4) were determined in Ref. 2 and the same definitions hold here. The radial equation (5) has general solutions $j_{L_n^m}(kr)$ and $y_{L_n^m}(r)$ where these are, respectively, the regular and irregular spherical Bessel functions. The condition (2) at

$r=r_0$ fixes the relative contributions of the two solutions and allows a general solution of (5) to be written in the form

$$\Psi=\sum_{n,m}\left(j_{L_n^m}(kr)-\frac{j_{L_n^m}(kr_0)}{y_{L_n^m}(kr_0)}\,y_{L_n^m}(kr)\right)\Theta_n^m(\mu)A_{nm}\,. \tag{6}$$

The coefficients A_{nm} are determined from the boundary condition

$$\Psi\underset{r\to\infty}{\sim}e^{i\vec{k}\cdot\vec{r}}+f(\mu,\varphi)\,e^{ikr}/r\,. \tag{7}$$

Following the analysis of Ref. 2, we get the result

$$A_{nm}=\Theta_n^m(-\eta)\exp[-i(\tfrac{1}{2}L_n^m-m)\pi]\times[1-ij_{L_n^m}(kr_0)/y_{L_n^m}(kr_0)]^{-1}\,, \tag{8}$$

where $\eta=\cos\xi$ and ξ is the angle between $\vec{k}$ and $\vec{\alpha}$. The resultant scattering amplitude, which is a function of the orientation η of the dipole, becomes

$$f(\mu,\varphi,\eta)=\frac{i}{2k}\sum_{n=0}^{\infty}\sum_{m=-\infty}^{\infty}\Theta_n^m(\mu)\,e^{im\varphi}\times[\Theta_n^m(\eta)-\Theta_n^m(-\eta)\,e^{-i(L_n^m-m)\pi}(1+i\,\delta_{L_n^m})^2(1-\delta_{L_n^m}^2)^{-1}]\,, \tag{9}$$

where

$$\delta_{L_n^m}=j_{L_n^m}(kr_0)/y_{L_n^m}(kr_0)\xrightarrow[kr_0<1]{}(kr_0)^{2L_n^m+1}\xrightarrow[n\to\infty]{}0\,.$$

For low-energy scattering and/or small r_0 such that $kr_0<1$, we note that

$$j_{L_n^m}(kr_0)/y_{L_n^m}(kr_0)\to(kr_0)^{2L_n^m+1}$$

as n becomes large. Furthermore, $L_n^m\to n$ as $n\to\infty$, thus the quantities $\delta_{L_n^m}\to0$ as n increases with the result that the terms in the expansion (9) of the scattering amplitude for the present modified dipolar field rapidly approach those for a point dipole.[2] The differential scattering cross section for a fixed dipole with orientation angle η,

$$d\sigma(\mu,\varphi,\eta)\,d\Omega=|f(\mu,\varphi,\eta)|^2\,d\Omega\,, \tag{10}$$

is quite complicated. In the case of a point dipole the differential cross section diverges in the forward direction with the result that the total scattering cross section also diverges.[2] This divergence results from contributions of terms of large n, m in the expansion, analogous to Eq. (9), of the scattering amplitude. In order to assess the contribution of the terms involving $\delta_{L_n^m}$, it is more convenient to obtain the total cross section by substituting (9) into (10) and integrating over $d\Omega$. Thus,

$$\sigma(\eta)=\frac{1}{4k^2}\times\sum_{n,m}\left(\Theta_n^{m*}(\eta)-\Theta_n^{m*}(-\eta)\,e^{i(L_n^m-m)\pi}\,\frac{(1-i\,\delta_{L_n^m})^2}{1+\delta_{L_n^m}^2}\right)\times\left(\Theta_n^m(\eta)-\Theta_n^m(-\eta)\,e^{-i(L_n^m-m)\pi}\,\frac{(1+i\,\delta_{L_n^m})^2}{1+\delta_{L_n^m}^2}\right). \tag{11}$$

The n, mth term in the double sum of series (11) differs from that for the point dipole through the added contribution

$$4(kr_0)^{2L_n^m+1}\{\Theta_n^m(\eta)\,\Theta_n^m(-\eta)\sin(L_n^m-m)\pi+[\Theta_n^m(-\eta)]^2(kr_0)^{2L_n^m+1}\}$$

from the repulsive core. For the point dipole ($\delta_{L_n^m}\equiv0$) the terms in the series go as $1/n^2$ for large n with the result that the double summation leads to a logarithmic divergence of σ. Since the contribution from the repulsive core diminishes as ϵ^{2n+1} (where $\epsilon=kr_0<1$) and since $n^2\epsilon^{2n+1}\to0$ as $n\to\infty$, the series (11) exhibits the same behavior for large n as that for the point dipole. Thus the divergence of the total scattering cross section is not changed in scattering by the modified dipolar field. Both problems lead to a divergent total cross section, and neither is due to a singularity at the origin. Furthermore, if the singularity is removed through some other form of finite dipole potential, Eq. (5) is still appropriate for large r and the present conclusions remain the same. We obtain this result in a different manner in the analysis which follows.

Now let us consider the general case of scattering from a finite dipolar system and investigate the fixed dipole limit of this problem. We start with a finite nonstationary rigid rotator system with dipolar charges $\pm q$ separated by a distance $R=2s$ and possessing a moment of inertia I about its center of mass. The general close-coupling formalism for an exact treatment of this problem has been presented by Arthurs and Dalgarno,[6] who give expressions for elastic and excitation cross sections in terms of transition matrix elements. In the close-coupling approach the rotational angular momentum of the dipole (designated by quantum number j) and the orbital angular momentum of the incident particle (designated by l) are coupled to give the total angular momentum $\vec{J}=\vec{j}+\vec{l}$ which is conserved. For scattering by a pure dipole field, rotational transitions $j\to j'$ are allowed only for $j'=j$, $j\pm1$.

Through utilization of the close-coupling formulation of Ref. 6, Itikawa and Takayanagi[7] have determined elastic and inelastic cross sections for low-energy electrons scattered by a finite dipolar system. They also show that for transitions $j\to j\pm1$, the higher partial-wave components of the cross sections become identical to the results from a similar angular momentum decomposition of the Born approximation.[7,8] (In the first Born approximation, the elastic cross section, $j\to j$, vanishes.[8,9] Elastic scattering proceeds via virtual excitations to rotational states $j\pm1$.)

Now we make the following observation. If one examines the Born higher-angular-momentum partial cross sections for inelastic (or superelastic) scattering from a point dipole[8] and compares these with the corresponding quantities for a finite dipole,[7] it is easily seen that these become equivalent for large enough total angular momentum J. If the cross section for a transition $j\to j'$ is written as

$$\sigma(j\to j')=\sum_{J=0}^{\infty}\sigma_J(j\to j')\ , \tag{12}$$

then the Born result for σ_J is[7]

$$\sigma_J^B(j\to j')=\frac{16\pi}{2j+1}\,\frac{k_{j'}}{k_j}\,(2J+1)\sum_l\sum_{l'}\Big|\langle j'\,l'\,J|\cos\theta|\,jlJ\rangle\times\int_0^\infty r^2 j_{l'}(k_{j'}r)\,j_l(k_jr)\,V_1(r)\,dr\Big|^2\ . \tag{13}$$

For the point dipole $V_1(r)=\mathfrak{D}/r^2$. For a finite dipole $V_1(r)=\mathfrak{D}r/s^3$ for $r<s$ and $V_1(r)=\mathfrak{D}/r^2$ for $r>s$, where s is the charge separation of the dipole. After noting that $l,\ l'=J\pm1$, it is obvious from the expression for σ_J^B that the discrepancy between the results for a finite and a point dipole rapidly vanishes as J becomes large, with the result that the series (13) exhibit the same convergence properties[10] for the two cases. Thus, we have the further statement that the higher-angular-momentum components of the cross section for $j\to j'$ transitions in the case of the finite and point dipole rigid rotators coincide.

Finally, we note that the cross sections for transition $j\to j\pm1$ for a point dipole rotator have been determined in the Born approximation by Takanagi[8] and can be written in closed form as

$$\sigma^B(j\to j+1)=\frac{8\pi}{3k^2}\left(\frac{\mathfrak{D}\,em}{\hbar^2}\right)^2\left(\frac{j+1}{2j+1}\right)\ln\left|\frac{k+k'}{k-k'}\right| \tag{14}$$

and

$$\sigma^B(j\to j-1)=\frac{8\pi}{3k^2}\left(\frac{\mathfrak{D}\,em}{\hbar^2}\right)^2\left(\frac{j}{2j+1}\right)\ln\left|\frac{k+k'}{k-k'}\right|\ . \tag{15}$$

Since

$$k'=\left[\frac{2m}{\hbar^2}\left(E-\frac{j(j+1)\hbar}{2I}\right)\right]^{1/2},$$

we note that the cross sections for transitions $j\to j\pm1$ diverge in the limit $I\to\infty$. Furthermore, by the argument given above, the same divergence occurs for a finite dipole. Finally, since the divergence is due to the contribution to the total cross section of a large number of partial-wave components (which converge only as J^{-1} when $I\to\infty$),[8,9] we can conclude that an exact treatment of the problem leads to the same divergence in the $j\to j'$ cross sections as that from the Born approximation. This follows from the earlier statement that the partial cross sections from an exact treatment of the problem rapidly approach those from the Born approximation as J becomes large.

From the argument just given we have a result which was earlier obtained in the Born approximation, namely, that in an exact treatment the cross sections for transitions $j\to j\pm1$ of a dipolar system become infinite in the limit of rotational degeneracy ($I\to\infty$). However, our concern in the present context is with the elastic cross sections for scattering from a fixed field source. Thus, we need to know the connection between the elastic scattering cross section from a system with fixed nuclei and those from a freely rotating system in the limit as $I\to\infty$. This connection has been provided in a recent paper by Chang and Temkin,[11] where it is shown that the expression for elastic scattering in the fixed nuclei approximation averaged over classical orientations of the internuclear axis is equivalent to the sum, in the limit $I\to\infty$, of the cross sections for transitions from a given rotational level j to all final rotational levels j'. Thus

$$\bar\sigma=\lim_{I\to\infty}\sum_{j'}\sigma(j\to j')\ , \tag{16}$$

where $\bar\sigma$ is the elastic cross section in the fixed nuclei approximation. Now if we return to the dipole problem, we see immediately that the theorem expressed in Eq. (16) leads to the result that the elastic cross section $\bar\sigma$ for scattering from a fixed dipole diverges as do the excitation (and the deexcitation) cross sections for the $I=\infty$ limit of the nonstationary dipole. Thus, the result obtained above in the modification of the Mittleman–von Holdt treatment of a point dipole is also true in the general case of elastic scattering by a fixed dipole in which the singularity does not appear; namely, the total cross section diverges. This result was surmised in a recent paper by Bottcher[12] and was shown to hold in the $E=0$ limit by Garrett.[13]

III. DIPOLAR SCATTERING BY TWO-CENTER COORDINATES

We noted earlier that Takayanagi and Itikawa[4] have performed calculations of total and differential scattering cross sections for low-energy electrons on a finite dipole which consisted of two point charges of opposite sign fixed at a distance R apart. Their finite results for total elastic scattering cross sections for this system are contrary to the conclusions just reached. The reason for this disparity can be revealed through a brief sketch of the formulation of the problem in prolate spheroidal coordinates.[3,4,14]

Define

$$\xi=\frac{r_A+r_B}{R}\ ,\quad \eta=\frac{r_A-r_B}{R}\ ,\quad\text{and}\quad \varphi\ ,$$

where r_A and r_B are the distances from the positions of the charge $+Ze$ (at point A) and $-Ze$ (at B), respectively, and φ is the azimuthal angle. In this coordinate system the Schrödinger equation for electron scattering by the dipolar system (of dipole moment $D=ZeR$) is separable. However, neither the "angular" η equation nor the "radial" ξ equation has exact solutions in terms of the familiar spheroidal wave functions which are appropriate for this coordinate system. Thus, in order to obtain two separated differential equations one must pay the price of finding solutions numerically for both equations.[3,4] Furthermore, analytic investigation of the problem is difficult in such a formulation. For our purposes the earlier more general formulation of the two-center scattering problem by Nagahara[14] is more convenient.

The Schrödinger equation in prolate spheroidal coordinates takes the form

$$[\mathcal{L}_\xi^m - \mathcal{L}_\eta^m + \kappa^2(\xi^2-\eta^2) - W(\xi,\eta)(\xi^2-\eta^2)]\Phi_m(\xi,\eta)=0\ , \tag{17}$$

where we have written the wave function

$$\psi(\xi,\eta,\varphi)=\Phi_m(\xi,\eta)e^{im\varphi}/(2\pi)^{1/2}$$

and have defined

$$\mathcal{L}_x^m=\frac{\partial}{\partial x}\left((x^2-1)\frac{\partial}{\partial x}\right)-\frac{m^2}{x^2-1}\ ,\quad x=\xi,\eta$$

$$W(\xi,\eta)=\frac{2m}{\hbar^2}\left(\frac{R}{2}\right)^2\ ,\qquad V=\frac{2\mathfrak{D}}{ea_0}\ \frac{\eta}{\xi^2-\eta^2}\ , \tag{18}$$

$$\kappa^2=\frac{2mE}{\hbar^2}\left(\frac{R}{2}\right)^2=k^2\left(\frac{R}{2}\right)^2 .$$

Here $\mathfrak{D}$ is the dipole moment of the target system and a_0 is the Bohr radius.

Following Nagahara we can expand the function Φ_m in terms of the complete set of orthonormal functions $N_{lm}(\eta)$:

$$\Phi_i^m(\xi,\eta)=\sum_l f_{il}^m(\xi)N_{lm}(\eta)\ . \tag{19}$$

The normalized angular spheroidal function N_{lm} is defined on the interval $-1\le\eta\le 1$ as the eigenfunction corresponding to the lth eigenvalue λ_l^m of the equation[15]

$$(\mathcal{L}_\eta^m+\kappa^2\eta^2)N_{lm}(\eta)=\lambda_l^m N_{lm}(\eta)\ , \tag{20}$$

where

$$\int_{-1}^1 N_{lm}(\eta)N_{l'm}(\eta)d\eta=\delta_{ll'}\ . \tag{21}$$

By substituting the expansion (19) into Eq. (17), multiplying by N_{lm}, integrating over the coordinate η, and making use of Eq. (20), we obtain

$$\frac{d}{d\xi}\left((\xi^2-1)\frac{d}{d\xi}\right)f_{il}^m(\xi)+\left(\kappa^2\xi^2-\frac{m^2}{\xi^2-1}-\lambda_l^m\right)f_{il}^m(\xi)=-\left(\frac{2e\mathfrak{D}}{a_0}\right)\sum_{l'}C_{ll'}^m f_{il'}^m(\xi)\ , \tag{22}$$

where $C_{ll'}$ is defined by

$$C_{ll'}=\int_{-1}^1 N_{lm}(\eta)\,\eta N_{l'm}(\eta)d\eta\ . \tag{23}$$

For a given value of m, there are an infinite number of coupled differential equations (22) for the "radial" functions f_{il}^m. This set of coupled equations has an infinite number of linearly independent solutions which are distinguished by the label i. From these solutions one may obtain a wave function which represents an incident wave plus a scattered wave expressed in spheroidal wave components. In order to define a cross section in terms of the usual phase shifts, use is made of the expansion[15]

$$e^{i\vec{k}\cdot\vec{r}}=2\sum_{m,l}(2-\delta_{m0})i^l N_{lm}(\cos\alpha)je_l^m(k,\xi)N_{lm}(\eta)\times\cos[m(\varphi-\beta)]\ , \tag{24}$$

where α, β are the polar and azimuthal angles of $\vec{k}$ relative to the dipole. The "radial" spheroidal functions $je_l^m(k,\xi)$ are solutions of Eq. (20) on $1\le\xi\le\infty$ and have asymptotic form

$$je_l^m(k,\xi)\sim[\sin(k\xi-\tfrac{1}{2}l\pi)]/k\xi\ . \tag{25}$$

The set of functions f_{il}^m which satisfy Eq. (21) can be written with asymptotic form

$$f_{il}^m(\xi)\sim B_{il}^m\,\frac{\sin(\kappa\xi-\frac{1}{2}l\pi+\Delta_{il}^m)}{k\xi}=B_{il}^m\left(e^{-i\Delta_{il}^m}\,\frac{\sin(\kappa\xi-\frac{1}{2}l\pi)}{\kappa\xi}+\sin\Delta_{il}^m\,\frac{e^{i(\kappa\xi-l\pi/2)}}{\kappa\xi}\right)\ . \tag{26}$$

Nagahara[14] has shown that a set of solutions with the required asymptotic behavior may be obtained from the set of functions $\Phi_i^m(\xi,\eta)$ of Eq. (19), where the f_{il}^m are obtained from (22) by introducing an infinite matrix D_{li}^m which is the inverse of the matrix $B_{il}^m e^{-i\Delta_{il}^m}$; that is,

$$\sum_i D_{ki}^m B_{il}^m e^{-i\Delta_{il}^m}=\delta_{kl}\ . \tag{27}$$

If the set of functions $\Phi_i^m(\xi,\eta)$ is transformed by the matrix D_{li}^m, then one obtains a set of solutions $\psi_l^m(\xi,\eta)$ with the required boundary condition

$$\psi_l^m(\xi,\eta)=\sum_i D_{li}\Phi_i^m(\xi,\eta)\sim\frac{\sin(\kappa\xi-\frac{1}{2}l\pi)}{\kappa\xi}N_{lm}(\eta)+\sum_{l'}\frac{2\gamma_{ll'}^m e^{i(\kappa\xi-\pi l'/2)}}{\kappa\xi}N_{l'm}(\eta)\ , \tag{28}$$

where

$$\gamma_{ll'}^m=\sum_i D_{li}^m B_{il'}^m\sin\Delta_{il'}^m\ . \tag{29}$$

The total cross section, averaged over all orientations of the dipole, is expressed as

$$\bar{\sigma}=\frac{4\pi}{k^2}\sum_m\sum_l\sum_{l'}(2-\delta_{m0})|\gamma^m_{ll'}|^2 . \quad (30)$$

We now examine the convergence of expansion (30) for the total elastic scattering cross section. The convergence property of the series (30) is determined by the products of terms D^m_{li}, $B^m_{il'}$, and $\sin\Delta^m_{il'}$. If we examine Eq. (27), which defines D^m_{li}, it is evident that for large l, where Δ^m_{il} approaches zero (at a rate to be determined below), the relationship (27) becomes

$$\sum_i D^m_{ki}B^m_{il}\cong\delta_{kl} .$$

Thus in the series expression for $\bar{\sigma}$ the sum of products $D_{li}B_{il'}$ is of the order of unity in the higher-order terms of Eq. (30) where $\sin\Delta^m_{il'}$ varies slowly with increasing l. The convergence is thus essentially determined by the behavior of the phase shifts $\Delta^m_{il'}$ in the triple sum over l, l', m. We thus examine their properties in some detail.

The lth partial-wave phase shift to Δ^m_{il} represents the asymptotic difference in phase between the solution f^m_{il} of Eq. (22) and the lth spheroidal radial function $je^m_l(k,\xi)$. The spheroidal function satisfies (22) when the right-hand side is set equal to zero. In order to determine the functional dependence of the phase shifts on the quantum number l, it is helpful to write the coupled set (22) in an uncoupled form. This may be done through the use of an "optical" potential.[16]

In order to simplify the notation, we temporarily drop the subscript i which distinguishes a particular set of solutions of the coupled set (22) from other linearly independent solutions of the same equations. We now write the equations for the components f^m_l (for given fixed m) in matrix notation.[16] For this purpose we define the matrices

$$H_{jk}=\left(\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}-\frac{m^2}{\xi^2-1}-\lambda^m_j\right)\delta_{jk}+\frac{2e\mathfrak{D}}{a_0}C^m_{jk} ,\quad j,k\neq l ,$$

$$\underline{\Upsilon}(\xi)=\begin{pmatrix} f^m_0(\xi)\\ f^m_1(\xi)\\ \vdots\\ f^m_{l-1}(\xi)\\ f^m_{l+1}(\xi)\\ \vdots\end{pmatrix} ,$$

$$\underline{C}=(2e\mathfrak{D}/a_0)(C^m_{l0},\ C^m_{l1},\ldots) , \quad (31)$$

$$\underline{C}^\dagger=\frac{2e\mathfrak{D}}{a_0}\begin{pmatrix}C^m_{l0}\\ C^m_{l1}\\ \vdots\end{pmatrix} .$$

With this notation the coupled equations represented by (22) become

$$(\mathfrak{L}^m_\xi+\kappa^2\xi^2-\lambda^m_l)f^m_l(\xi)=-\underline{C}\,\underline{\Upsilon}(\xi) , \quad (32)$$

$$(\underline{H}+\kappa^2\xi^2)\underline{\Upsilon}(\xi)=-\underline{C}^\dagger f^m_l(\xi) . \quad (33)$$

In Eqs. (32) and (33) we have singled out the lth distorted spheroidal wave f^m_l which we now obtain in an uncoupled form. To achieve this we solve (33), formally, in terms of f^m_l, i.e.,

$$\underline{\Upsilon}(\xi)=-[1/(\underline{H}+E^{(+)}\xi^2)]\underline{C}^\dagger f^m_l , \quad (34)$$

where $E^{(+)}=\kappa^2+i\epsilon$; $\epsilon\to 0^{(+)}$. By inserting (34) into Eq. (32) we obtain an equation for $f^m_l(\xi)$ in the form[16]

$$\left(\mathfrak{L}^m_\xi+\kappa^2\xi^2-\lambda^m_l-\underline{C}\frac{1}{\underline{H}+E^{(+)}\xi^2}\underline{C}^\dagger\right)f^m_l(\xi)=0 . \quad (35)$$

Thus we have an uncoupled equation for f^m_l which contains an "optical potential" operator $\underline{C}(\underline{H}+E^{(+)}\times\xi^2)^{-1}\underline{C}^\dagger$. In order to discuss the properties of the optical potential and the resultant phase shift, it is convenient to expand the inverse operator in terms of the eigenfunctions of $\underline{H}$. In general, the spectrum of $\underline{H}$ will consist of a discrete part and a continuum. We specify these eigenfunctions as

$$(\underline{H}+\mathcal{E}_n\xi^2)\underline{\Upsilon}_n=0 \quad (36)$$

for the discrete spectrum, and

$$(\underline{H}+\epsilon\xi^2)\underline{\Upsilon}_\epsilon=0 \quad (37)$$

for the continuum. If we now expand the inverse operator in terms of this basic set, we obtain

$$V_0=\underline{C}\frac{1}{\underline{H}+E^{(+)}\xi^2}\underline{C}^\dagger =\sum_n\frac{\underline{C}\,\underline{\Upsilon}_n\rangle\langle\underline{\Upsilon}^\dagger_n\underline{C}^\dagger}{k^2-\mathcal{E}_n}+\int\frac{\underline{C}\,\underline{\Upsilon}_{\epsilon'}\rangle\langle\underline{\Upsilon}^\dagger_{\epsilon'}\underline{C}^\dagger}{E^{(+)}-\epsilon'}d\epsilon' . \quad (38)$$

With this notation, Eq. (35) becomes

$$\frac{d}{d\xi}(\xi^2-1)\frac{d}{d\xi}f^m_l-\left(\frac{m^2}{\xi^2-1}-\kappa^2\xi^2+\lambda^m_l+V_0\right)f^m_l=0 . \quad (39)$$

Thus, for each of the members of the coupled set (22) we may write an uncoupled equation of the form (39) from which a phase shift may be determined through asymptotic comparison with the lth spheroidal wave je^m_l.

In the optical potential V_0 the bound-state basis functions $\underline{\Upsilon}_n$ are exponentially decreasing for large ξ; thus the asymptotic form is determined by the second term of (38). The continuum contribution contains the functions $\underline{\Upsilon}_\epsilon$ which, from Eq. (37), go asymptotically as spheroidal waves. In addition, we have the constant row and column matrices $\underline{C}$ and $\underline{C}^\dagger$. Upon examination of the asymptotic form of the term $V_0f^m_l$ in Eq. (39), we note that the principal value in the integral over $d\epsilon'$ will be contributed at $\epsilon'=E$ and the nonlocal operator $\int\underline{\Upsilon}^\dagger_{\epsilon'}\underline{C}^\dagger f^m_l d\xi$

is a constant times a spheroidal function. The functions $\Upsilon_{\epsilon'}$ are normalized to unit amplitude; thus the magnitudes of the terms in (38) are determined by the constant matrices $\underline{C}$ and $\underline{C}^\dagger$.

We can readily determine the properties of the constants $C_{ll'}^m$ defined by (23) and of the row matrix $\underline{C}$ through a limiting process. For this purpose we note that in the limit $k \to 0$ the angular spheroidal functions, $N_{lm}(\eta)$, become identical to the normalized associated Legendre polynomials $\mathcal{P}_l^m(\eta)$. In this case the properties of the Legendre polynomials lead to the result that

$$\lim_{k\to 0} C_{ll'}^m = \begin{cases} \left(\dfrac{(l+m)(l-m)}{(2l-1)(2l+1)}\right)^{1/2} \delta_{l',l-1} \\ \left(\dfrac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right)^{1/2} \delta_{l',l+1} \end{cases} . \quad (40)$$

For low-energy scattering where the value of k is small the matrix elements $C_{ll'}^m$ defined by Eq. (23) will be largest for $l' = l \pm 1$ and will not depart significantly from expression (40). Thus, only two terms in the matrix $\underline{C}$ are significantly different from zero, and these exhibit the l dependence of Eq. (40).

For large values of ξ, Eq. (39) reduces to the form

$$\frac{d^2}{d\xi^2} f_l^m + \frac{2}{\xi}\frac{d}{d\xi} f_l^m - \left(\kappa^2 - \frac{\lambda_l^m + V_0}{\xi^2}\right) f_l^m = 0 . \quad (41)$$

This is Bessel's equation; thus Eq. (41) has solutions of the form

$$f_l^m(\xi) \sim \xi^{-1/2} J_{\rho+1/2}(\kappa\xi + \delta_l) \sim [\sin(\kappa\xi - \tfrac{1}{2} l\pi + \delta_l)]/\kappa\xi , \quad (42)$$

where $\rho(\rho+1) = \lambda_l^m$ and δ_l is a phase shift due to V_0. However, by the argument just given, the term $V_0 f_l^m$ goes asymptotically like a spheroidal wave with a multiplicative l-dependent constant which is determined by Eq. (38). Thus the solutions of Eq. (41) may also be written as

$$f_l^m(\xi) \sim \xi^{-1/2} J_{\nu+1/2}(\kappa\xi) \sim \{\sin[\kappa\xi - \tfrac{1}{2} l\pi - \tfrac{1}{2}\pi(\nu - l)]\}/\kappa\xi , \quad (43)$$

where $\nu(\nu+1) = \lambda_l^m + v_0$, and the constant v_0 is determined by the exact asymptotic form of the second term in Eq. (38). A solution in the form (43) is possible because of the fact that the term V_0/ξ^2 has the same asymptotic functional form as that of the centrifugal term λ_l^m/ξ^2. We cannot obtain the constant v_0 analytically, but we note from the previous analysis that the amplitude of V_0 in (38) is approximately proportional to $\underline{C}\,\underline{C}^\dagger$ and that the elements of $\underline{C}$ and $\underline{C}^\dagger$ are negligible but for those of Eq. (40). Thus the l dependence of V_0 and consequently that of the shift v_0 in the Bessel functions, goes as the product of terms in Eq. (40).

We are now in a position to determine the l dependence of the phase shift Δ_l^m for large values of l. The eigenvalues λ_l^m of Eq. (20) have the properties that $\lambda_l^m \to l(l+1)$ for large l. Thus, the solutions of asymptotic form (43) yield the result

$$\nu(\nu+1) \underset{l\to\infty}{\sim} l(l+1) + v_0 . \quad (44)$$

From (43) and (44) we get a result analogous to that for scattering from a spherically symmetric r^{-2} potential,[5] namely,

$$\Delta_l^m = \tfrac{1}{2}\pi(\nu - l) \sim \tfrac{1}{2}\pi v_0/(2l+1) . \quad (45)$$

Finally, from the previous argument the l dependence of v_0 goes as products of terms in expression (44), e.g.,

$$v_0 \sim \left(\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)}\right) + \cdots . \quad (46)$$

Thus, we have a final l dependence of phase shift

$$\Delta_l^m \sim \frac{\pi}{2}\left(\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)(2l+1)}\right) + \cdots \quad (47)$$

or other similar products of the same form. Thus, for very large l the phase shift goes as

$$\Delta_l^m \sim 1/(2l+1) . \quad (48)$$

This slow decrease in Δ_l^m is similar to that for the case of a spherically symmetric potential.[5] In fact, if we now return to expression (30) for the total elastic scattering cross section and use the result (48), we see, after interchanging the sums over l and m, that the sum diverges logarithmically. Thus, an exact treatment of charged-particle scattering by a finite dipole leads to a divergent total elastic cross section. The finite values obtained by Takayanagi and Itikawa for the total cross section resulted from truncation error in numerically evaluating the first few terms of a divergent series.

IV. CONCLUSIONS

It is very interesting that the dipolar inverse square potential, which is over all neither attractive nor repulsive, leads to a sufficient distortion of an incident plane wave to yield a divergent scattering cross section as does the spherically symmetric inverse square potential. The divergence results from the long range of the interaction and is a general property of the field, independent of the value of the dipole moment of the field source. We have shown how this result follows from the fixed dipole limit of scattering from a nonstationary dipolar system with finite moment of interia, and how the same conclusions follow from a careful inspection of the more difficult, but exact, treatment of scattering from a fixed dipolar system in prolate spheroidal coordinates.

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[1]S. Altshuler, Phys. Rev. 107, 114 (1957).

[2]M. H. Mittleman and R. E. von Holdt, Phys. Rev. 140, A726 (1965).

[3]M. Shimizu, J. Phys. Soc. Japan 18, 811 (1963).

[4]K. Takayanagi and Y. Itikawa, J. Phys. Soc. Japan 24, 160 (1968).

[5]N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 3rd ed. (Oxford U.P., London, 1965), p. 41.

[6]A. M. Arthurs and A. Dalgarno, Proc. Roy. Soc. (London) A256, 540 (1960).

[7]Y. Itikawa and K. Takayanagi, J. Phys. Soc. Japan 26, 1254 (1969).

[8]K. Takayanagi, J. Phys. Soc. Japan 21, 507 (1960).

[9]O. Crawford, A. Dalgarno, and P. B. Hays, Mol. Phys. 13, 181 (1967).

[10]The difference between the matrix elements for the point dipole and finite dipole goes as

$$\int_0^{r_0} r^2 j_{l'}(k_j r) j_l(k_j r) \frac{1}{r^2}\, dr - \int_0^{r_0} r^2 j_l(k_j r) j_{l'}(k_j r) \frac{r}{s^2}\, dr \rightarrow \frac{(kr_0)^{l+l'+1}}{k(l+l'+1)} \left(1 - (kr_0)^3 \frac{l+l'+1}{l+l'+4}\right) \rightarrow 0$$

as $l,\ l' \rightarrow \infty$. Since $l^2 (kr_0)^{l+l'+1} \rightarrow 0$ as $l \rightarrow \infty$, Eq. (13) exhibits the same convergence properties for the point dipole and finite dipole problems.

[11]E. S. Chang and A. Temkin, Phys. Rev. Letters 23, 399 (1969).

[12]C. Bottcher, Mol. Phys. 19, 193 (1970).

[13]W. R. Garrett, Phys. Rev. A 3, 961 (1971).

[14]G. Nagahara, J. Phys. Soc. Japan 8, 165 (1953).

[15]P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 1502. The normalized spheroidal function defined here is related to that of Morse and Feshbach, denoted by $S_{jm}(\eta)$, through the relation $N_{jm}(\eta) = \Lambda_{jm}^{-1/2} S_{jm}(\eta)$, where $\Lambda_{jm} = \int_{-1}^{1} S_{jm}(\eta) S_{jm}(\eta)\, d\eta$.

[16]H. Feshbach, Ann. Phys. (N.Y.) 5, 357 (1958).

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Quantum-Mechanical Calculation of Cross Sections for Inelastic Atom-Atom Collisions. I. Inelastic $2\,^3S \rightarrow 2\,^3P$ Collisions between Metastable and Ground-State Helium Atoms*

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A quantum-mechanical two-state close-coupling calculation of the inelastic cross section for the $2\,^3S \rightarrow 2\,^3P$ excitation has been carried out for collisions between $2\,^3S$ metastable and ground-state helium atoms in the center-of-mass (c.m.) energy range 5–500 eV. The calculations were carried out in both the diabatic and adiabatic representations using two single-configuration valence-bond molecular wave functions and the corresponding adiabatic linear combinations, respectively. Both representations, as expected, gave identical results. In the diabatic representation, the coupling matrix element was found to be extremely large, resulting in a strong avoided crossing of the corresponding adiabatic potential curves and very small inelastic cross sections for energies $E \lesssim 100$ eV (c.m.), but increasing to a value of about 4×10^{-16} cm^2 at 500 eV (c.m.), The semiclassical Stueckelberg-Landau-Zener approximation was found to be very poor at all energies considered. The JWKB distorted-wave approximation was found to be fairly good at energies $E \gtrsim 400$ eV (c.m.).

I. INTRODUCTION

A. Theoretical Background

The theory of atom-atom collisions is among the most complicated problems of atomic and molecular physics and has received the attention of researchers for some time.[1-3] In high-energy collisions, a natural assumption is that the atomic states are relatively unperturbed during the collision. In this case, one may describe elastic scattering essentially as potential scattering from the first-order interaction of the atomic collision partners, and inelastic scattering as an impulsive transition between undistorted atomic states. If the coupling is weak, the Born approximation or distorted-wave method may be applied.

Further, at these high energies, the trajectories of heavy particles are fairly well described classically and an impact-parameter description of the scattering is meaningful. The inelastic process, however, involves transfer of momentum and energy to the bound electrons and is not classical. Hence, some uncertainty always exists in the description of the excitation mechanism itself. Considerable simplification results if in addition one assumes a straight-line path, the semiclassical analog of the Born approximation.

These semiclassical approaches are, of course, time-dependent in nature. However, a time-independent semiclassical analysis is possible via the eikonal approximation, for example, which in a partial-wave analysis of a single-channel scatter-