Scattering by a dipolar system: Divergence of cross sections at the critical moment for a point dipole rotor

W. R. Garrett

Chemical Physics Section, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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It is shown that the quantum-mechanical problem of charged-particle scattering by a point-dipole rotor has pathological behavior at and above the critical dipole moment wherein all partial-wave components of the solution become undefined. The total elastic and momentum-transfer cross sections diverge at the critical moment, and, at energies above thresholds, scattering in inelastic channels behaves similarly. Clarifications are made of some existing contradictions in the literature on the quantum mechanics of continuum states for dipolar systems.

I. INTRODUCTION

The interactions of electrons with polar molecules form an interesting subset of problems in chemical physics; particularly from the standpoint of molecular theory where a number of the features of the quantum mechanics follows directly from the long-range nature of the electron-dipole interaction potential. Indeed, conclusions that can be drawn from the behavior of discrete and continuum solutions for a charged particle interacting with a "pure-dipole" potential, or with a simple dipole rotor, can in certain instances be carried over to the theoretical treatment of electron interactions with real polar molecules. Moreover, in the theoretical treatment of specific polar systems, approximations can often be made such that a given portion of the problem may be conveniently approximated by a result from a simple dipolar system.[1] Thus, the discrete and continuum solutions for a charged particle in the field of a stationary dipole potential and those for a charged particle interacting with a dipole rotor are of interest in the context of theoretical studies of polar molecules in addition to their interest as basic "textbook" problems in quantum mechanics. Without belaboring the points unduly, it is beneficial to the present discussion to note several features of scattering solutions for the problems mentioned above.

Massey[2] first established some of the properties of the cross sections for scattering by a dipolar potential. He obtained the Born approximation result for inelastic electron scattering by a symmetric top dipole rotor. He noted that the first Born cross section for elastic scattering by a pure-dipole rotor vanishes and that one should expect inelastic cross sections for real polar molecules to be much larger than the elastic component of the total scattering cross section. Much later, Takayanagi[3] extended the Massey result for scattering by a linear point-dipole rotor. He obtained closed-form expressions in the first Born approximation for inelastic, $\sigma(j \to j+1)$ and superelastic, $\sigma(j \to j-1)$ scattering cross sections (j = rotational quantum number of the dipole rotor).

$$\sigma_{\text{Born}}(j \to j+1) = \frac{8\pi}{3k^2}\left(\frac{DeM_e}{\hbar^2}\right)^2 \frac{j}{2j+1} \ln\left|\frac{k+k'}{k-k'}\right| \quad (1)$$

and

$$\sigma_{\text{Born}}(j \to j-1) = \frac{8\pi}{3k^2}\left(\frac{DeM_e}{\hbar^2}\right)^2 \frac{j+1}{2j+1} \ln\left|\frac{k''+k}{k''-k}\right| , \quad (2)$$

where k is the initial wave vector of the electron, k' and k'' are the final wave vectors after inelastic or superelastic scattering, respectively, and D is the dipole moment of the linear point-dipole rotor.

Altshuler[4] considered the problem of electron scattering by a *fixed,* point dipole. He also worked within the Born approximation and obtained closed-form solutions for the differential cross sections $d\bar{\sigma}_{\text{Born}}$ and the diffusion or momentum-transfer cross section $\bar{\sigma}_{\text{Born}}$ (averaged over possible orientations of the fixed-dipole scatter). His analysis gave

$$d\bar{\sigma}_{\text{Born}}(\theta) = \frac{4}{3}\left(\frac{DeM_e}{\hbar^2}\right)^2 \frac{1}{2k^2(1-\cos\theta)} \quad (3)$$

and

$$\sigma_{\text{Born}} = \frac{8\pi}{3}\left(\frac{DeM_e}{\hbar^2}\right)^2 \frac{1}{k^2} . \quad (4)$$

Although Altshuler did not discuss the total Born scattering cross section, note that his result in Eq. (3) yields a logarithmic divergence for $\sigma_{\text{Born}}^{\text{total}}$ when integrated over scattering angle θ.

In a later study, Mittleman and Von Holdt[5] (MVH) obtained *exact* solutions for the scattering of an electron by a point dipole of fixed orientation. The exact result was compared with the earlier Born approximation result[4] for the same problem. The exact result for the total cross section again diverged and the momentum-transfer cross section was larger than the corresponding Born approxi-

mation result. Also, a new feature was discovered for the stationary point-dipole problem; the momentum-transfer cross section *also* diverged at a critical dipole moment of $0.639ea_0$ and remained undefined at larger values of D. The point dipole potential

$$V(r) = -(eD/r^2)\cos\theta$$

was thus shown to lead to the same "fall to the center" behavior as that for the spherically symmetric r^{-2} potential,[6] when the strength of the interaction exceeded a critical value. However, it was later shown by the present author[7] that in the exact treatment of the scattering problem, the divergence of the total cross section was produced by the long range of the fixed-dipole potential, independent of the magnitude of $D \neq 0$ or the form of the interaction near $r = 0$, but that the momentum-transfer cross section is well defined for all D in the absence of the fall to the center feature of the point dipole.

Subsequent to the paper by MVH,[5] several authors[8-13] demonstrated that the critical moment D_c for the fixed-dipole potential divided the eigenvalue spectrum of the electron-dipole quantum-mechanical problem into two classes (zero bound states for $D < D_c$ and an infinite number for $D > D_c$), and Levy-Leblond and Provost[14] (LLP) argued that the scattering cross sections for real polar molecules would show singular behavior at the critical moment, independent of the short-range form of the potential or of rotational degrees of freedom of the molecular target system. Their argument was shown to be incorrect for a finite fixed[7]- or non-stationary[15,16]-dipole scatterer.

In the following section we show that the point-dipole rotor problem can be transformed to coincide with the stationary point-dipole problem as $r \to 0$, and the divergences which occur due to pathological behavior of the solutions at the origin of the point-dipole potential reoccur for the point-dipole rotor.

II. EXACT TREATMENT OF SCATTERING BY A POINT-DIPOLE ROTOR

The problem of electron scattering by a point dipole of fixed orientation provides the necessary basis for demonstrating new features of the problem of interest here. Thus, we note that the fixed-dipole scattering problem is described by[5]

$$(\nabla^2 + k^2 + \vec{\alpha}\cdot\vec{r}/r^3)\psi(\vec{r}) = 0\,, \tag{5}$$

where $\vec{\alpha} = 2eM_e\vec{D}/\hbar^2$ and $k^2 = 2M_eE/\hbar^2$. We make use of the fact that this problem is separable in spherical polar coordinates r, μ, ϕ ($\mu = \cos\theta$) with solutions whose analytic properties have been demonstrated.[5,7,13] Thus if one writes

$$\psi(\vec{r}) = r^{-1}R(r)\theta(\mu)e^{im\phi}\,, \tag{6}$$

then Eq. (5) yields the separated equations

$$\left(\frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu} - \frac{m^2}{1-\mu^2} + \alpha\mu + L_n^m(L_n^m+1)\right)\theta_n^m(\mu) = 0 \tag{7}$$

and

$$\left(\frac{d^2}{dr^2} + k^2 - \frac{L_n^m(L_n^m+1)}{r^2}\right)R_n^m(r) = 0\,. \tag{8}$$

The condition that ψ be single valued and finite requires that m be an integer and that L_n^m be restricted to certain allowed values, obtainable from Eq. (7).

The solution of Eq. (8) which is finite at the origin is the spherical Bessel function $rj_{L_n^m}(kr)$. In fact, the equation is identical in form to the radial equation for the scattering problem involving a spherically symmetric r^{-2} potential. This equation is well known[6] to admit solutions only if $L_n^m(L_n^m+1) > -\frac{1}{4}$ (independent of the value of k^2). This results in an upper limit on D such that $D < 0.639ea_0$ for the existence of permissible solutions. For larger D the lowest L_n^m component of the solutions fall to the center, i.e., they oscillate an infinite number of times as $r \to 0$, and the boundary condition at the origin cannot be specified.[5,6,13] This behavior causes the momentum-transfer cross section to become undefined for supercritical point-dipole scattering. We make use of the properties of the above solutions in the following discourse.

To make the connection between the fixed-dipole and the dipole rotor problems, solutions are needed to the above problem in the form of the coupled equations that result from an expansion of the wave function in angular-momentum eigenfunctions. That is, if we choose alternatively to replace the expression in Eq. (6) by

$$\psi(\vec{r}) = \sum_{lm} r^{-1}F_{lm}(r)Y_l^m(\theta,\phi)\,, \tag{9}$$

the Schrödinger equation then leads to the set of coupled radial equations

$$\left(\frac{d^2}{dr^2} - l(l+1)/r^2 + k^2\right)F_{lm}(r) = \frac{\alpha}{r^2}\sum_{l'=l\pm1}\langle l'm|\cos\theta|lm\rangle F_{l'm}(r)\,. \tag{10}$$

The angular equation is in this case the equation for the spherical harmonics. It is similar to Eq. (7) but with the $\alpha\mu$ term missing and with $L_n^m(L_n^m+1)$ replaced by $l(l+1)$.

The inhomogenous coupled Eqs. (10) that result from the use of a spherical harmonic representation of the scattering function (9) are more com-

plicated than the Bessel equation (8) which results from the use of representation (6). Thus although the analytic properties of the set (10) are not so easily established, we know from the equivalence of the problem in the two representations that the coupled Eqs. (10) also fall to the center at $D=D_c$. In fact the functions $F_{lm}(r)$ are easily expressed as sums over the functions $R_n^m(r)$ and vice versa.

Now we consider the equation for a point-dipole *rotor* expressible in the form

$$\left(H_R-\frac{\hbar^2}{2m}\nabla_r^2-\frac{e\vec{D}\cdot\vec{r}}{r^3}\right)\Psi(\vec{r},\hat{D})=E\Psi(\vec{r},\hat{D}), \tag{11}$$

where H_R is the rotational Hamiltonian for the rotor

$$H_R\,Y_j^m(\hat{D})=j(j+1)\hbar^2/2I\,Y_j^m(\hat{D}). \tag{12}$$

Here I is the moment of inertia of the rotor which has energy $j(j+1)\hbar^2/2I$ in rotational state j. By forming the coupled spherical harmonics

$$Y_j^{JM}(\hat{r},\hat{D})=\sum_{m_j}\sum_{m_l}(jm_j lm_l|jlJM)Y_j^{m_j}(\hat{D})Y_l^{m_l}(\hat{r}), \tag{13}$$

which are eigenfunctions of the total angular momentum $\vec{J}=\vec{j}+\vec{l}$ and z component $M=m_j+m_l$, one can expand the total wave function for the electron-rotor system in the form

$$\Psi(\vec{r},\vec{D})=\sum_j\sum_l Y_{jl}^{JM}(\hat{r},\hat{D})U_{jl}^J(r)/r \tag{14}$$

and reduce Eq. (11) to the following set of reduced radial equations:

$$\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k_{jj'}^2\right)U_{jl}^J(r)$$

$$=\frac{\alpha}{r^2}\sum_{j'l'}\langle jl;J|\cos\theta_{rD}|j'l';J\rangle U_{j'l'}^J(r). \tag{15}$$

In this set of coupled equation $k_{jj'}^2=(2M_e/\hbar^2)\times[E_j-j'(j'+1)\hbar^2/2I]$ where E_j is the initial energy of the system (we consider scattering from a rotor initially in the ground state) and θ_{rD} is the angle between $\vec{r}$ and $\vec{D}$.

We can now use two facts relating to the set (15) which will establish that these equations exhibit pathological behavior at $D=0.639ea_0$ identical to that of Eqs. (8) and (10) which describe the simple point-dipole problem. First, in the region near the origin the energy terms k^2 can be neglected as compared to the divergent r^{-2} contributions in both sets of equations. Second, we make use of a property demonstrated in Ref. 7; namely, that in the instance where differences between k^2 and $k_{jj'}^2$ can be ignored for all jj' the set (15) of coupled equations can be transformed identically to the set (10) for the fixed dipole. In Ref. 7 this transformation was achieved in the $I\to\infty$ limit where the energies become degenerate. Here we can carry the exact same analysis through for the point-dipole rotor in the $r\to 0$ limit because the r^{-2} singularity obviates any differences in the equations due to the rotational spacings (i.e., the kinetic energy terms can be ignored). Thus, the analysis is similar to that of Ref. 7 as is shown in the Appendix. In this limit, the two sets of solutions are connected through the relation

$$\lim_{r\to 0}\left(F_{lm}(r)-\sum_j[(2j+1)/4\pi]^{1/2}(j0lm|jlJm)U_{jl}^J(r)\right)=0, \tag{16}$$

where $(j0lm|jlJM)$ is a Clebsch-Gordan coefficient. Thus the solutions to Eq. (15) behave identically to those of Eq. (10) at $r=0$. We know that the solutions to Eq. (10) fall to the center at $D=0.639ea_0$ because they are equivalent to the formulation in Eqs. (5)–(8) where this property can be shown analytically. Moreover, the pathological behavior occurs for all values of J, thus all partial waves become undefined at $D=D_c$.[17]

The above proof follows readily from the known behavior of the simple dipolar quantum problem. In the regime where $D<D_c$ one can also solve the set (15) directly by numerical integration. However, a fairly serious complication arises in this instance since the boundary condition at the origin is troublesome for the point-dipole potential. If one follows the usual practice of writing $U(r)\sim ar^s$ for the solutions to the coupled equation as $r\to 0$, it is necessary, in order to specify s, to solve an infinite matrix equation or a continued series of higher order differential equations. If, for example, the matrix is truncated to two terms one gets as permissible solutions,

$$s=\tfrac{1}{2}\pm\{\tfrac{1}{4}+[1-(1+D^2/3\sqrt{3})^{1/2}]\}^{1/2}.$$

The two term formula yields a fall to the center at $D=0.85ea_0$ (instead of the proper value $0.639ea_0$). By expanding the number of coupled equations (and thus the order of the matrix) one could, in principle, obtain D_c directly from the matrix solution to any desired level of accuracy. One finds again that the boundary condition at the origin cannot be met for $D\geq D_c$, with the result that the coupled equations cannot be solved. However, the above proof obviates any need of dealing with the problem of determining D_c through this method.

III. CROSS SECTIONS

The implications of the present results for scattering cross sections of a point-dipole rotor are fairly obvious. The pathological oscillatory behavior of the wave function at the origin for $D\geq D_c$

means that the boundary condition at $r=0$ cannot be specified when $D \geq D_c$. This condition prevails for all scattering energies and for all values of the total angular momentum J. Indeed, at energies below the first inelastic threshold each of the partial wave components, $\sigma^J(0,0)$ of the elastic scattering cross section will attain its maximum permissible value $(4\pi/k^2)(2J+1)$ as $D \to D_c$ from below. Thus, both the total cross section *and* the momentum-transfer cross section diverge at D_c. Since one of the necessary boundary conditions for specifying the scattering matrix cannot be met, the inelastic and superelastic scattering cross sections also become undefined for supercritical moments. Moreover, since dipole supported resonances are sure to occur at values of D which are somewhat less than that required to sustain a true bound state,[18] we know that cross sections for a given energy, when determined as a function of dipole moment, will show "resonant" behavior for some values of $D<D_c$, and that such oscillations in the calculated cross sections will occur at different values of D for various J and I.[16] It is tutorially interesting to plot the partial-wave cross sections for fixed energy as a function D, analagous to the plot of $\bar{\sigma}_m(\mu)$ given by Mittleman and Von Holdt[5] for the stationary point dipole. We show samples of such results in Figs. 1, 2, and 3, where the partial cross sections $\sigma^J(j,j')$ are shown for 0.03-eV electrons scattered from a point-dipole possessing moment of inertia $I=1\times 10^5 M_e a_0^2$. We note that the $J=0$ component of the elastic cross section rises monotonically toward its maximum $(4\pi/k^2)$ at $D=D_c$ and the inelastic S-wave component is a smooth function of D. However, as can be seen in Figs. 2 and 3 the $J=1$ components of $\sigma(0,0)$ and $\sigma(0,1)$ increase smoothly with D until

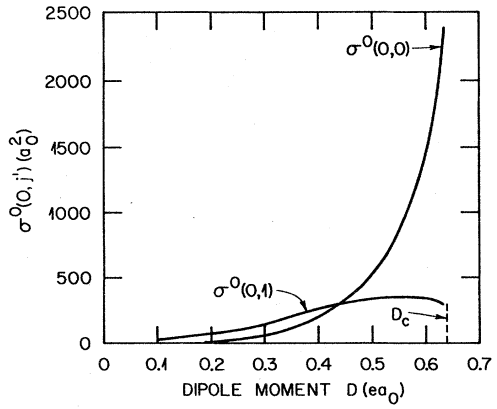

FIG. 1. Lowest angular-momentum ($J=0$) component of the elastic $\sigma(0,0)$ and rotational excitation $\sigma(0,1)$ cross sections for 0.03-eV electrons on a point-dipole rotor with moment of inertia $I=1\times 10^5 m_e a_0^2$.

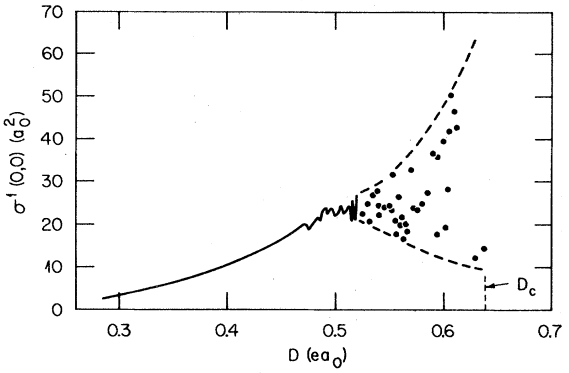

FIG. 2. The $J=1$ component of $\sigma(0,0)$. Energy and target system as in Fig. 1. For dipole moments greater than $0.52ea_0$ the oscillations become too closely spaced to be shown on the figure. The dotted lines are drawn to show the approximate range within which the $J=1$ component of the cross section varies as $D \to D_c$.

resonances set in as the dipole moment approaches D_c (in the present instance above $\sim 0.45ea_0$). This behavior is not unexpected in view of the recent proof by the present author[17] that the critical dipole moments for the excited states of the system under consideration all collapse back to the value of $0.639ea_0$.[19] Thus, the point-dipole rotor has, as $D \to D_c$, an infinite number of states, for each value of J, which can have associated with them scattering resonances in all open channels. We know from earlier results[18] that in $J>0$ channels resonances will appear at values of D less than those necessary to sustain a real bound state. In the present instance the oscillations in the cross sections are associated with the acquisition of additional nodes in the radial functions as $D \to D_c$. In the results of Figs. 2 and 3 the separations between the cross sectional maxima and minima as

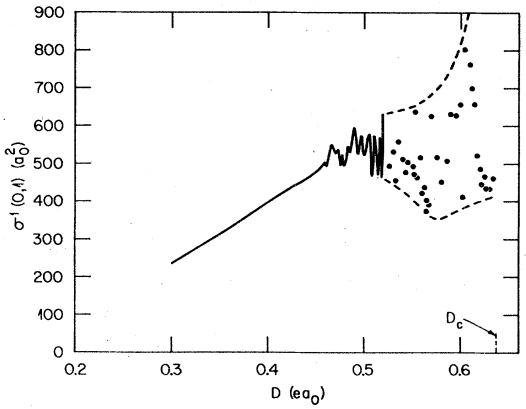

FIG. 3. The $J=1$ component of $\sigma(0,1)$ labeling as in Fig. 2.

a function of D get progressively smaller as D approaches D_c, becoming too closely spaced to be shown on the figures, and too costly to calculate on a grid sufficiently small to follow the behavior as $D \to D_c$. We show several data points for values of D lying between 0.52 and $0.639ea_0$ which are intended to indicate the magnitudes of the oscillations in $\sigma^J(j,j')$ as $D \to D_c$. Sample calculations demonstrated that, as expected,[19] such oscillatory behavior is also present for $J>1$. In the higher partial-wave contributions the individual oscillations are shifted further toward D_c with increasing values of J.[20,21]

Here a few useful comments can be made concerning some points made in previous papers on the subject of critical scattering of electrons by polar molecules. In the study of Levy-Leblond and Provost[14] it was argued that the cross sections would be finite but possess an infinite slope at $D = D_c$, independent of the behavior of the potential at $r=0$, and that the behavior would not be modified by the rotational structure of the molecule. This argument has already been shown to be wrong for scattering by a polar molecule or a finite polar rotor.[15,16] For the special case of a point-dipole rotor the conclusion that the cross section behaves badly at the critical moment is partially correct, but not exactly for the reason stated by LLP. The fall to the center does *not* occur *only* for the lowest partial wave as stated in Ref. 14. In fact, it is quite interesting that the dipole coupling between rotational and orbital angular momenta is such that each and every partial wave (which necessarily contains an $l=0$ term in the coupled radial equations), allows the electron to fall to the center, with a transfer of the angular momentum to the nuclei (i.e., the collapse could be characterized as occurring through the component of the coupled equations with $l=0$, $j=J$).[22] Thus, the behavior of the cross sections for the point dipole is "worse" than that described in Ref. 14, but as mentioned before, for a finite rotor the behavior at D_c is quite normal. On the other hand, Bottcher[23] argued that the cross sections would be "well behaved" for scattering by a supercritical field, even if the lowest-n partial waves were to collapse into the origin. Here it was not recognized that *none* of the partial waves misbehaves for a finite dipole rotor but *all* of them behave badly for a point-dipole rotor. Thus, the analysis of Ref. 23 is not appropriate for scattering by either type of dipole scatterer. For completeness we again note that a calculation by Takayanagi and Itikawa[24] of a finite cross section for electron scattering by a fixed-dipolar target system was incorrect in that a divergent series was truncated to yield a finite result.[7]

IV. CONCLUDING REMARKS

From the above discussion it is apparent that the problem of charged-particle scattering by a dipolar target system has interesting subtleties and a confusing history. The set of results represented by scattering from finite and point-dipole fields, from fixed and freely rotating target systems, and by Born approximation and exact treatments of each of these problems happens to cover all possible combinations of convergent and nonconvergent results for momentum-transfer and total scattering cross sections. To wit:

A. Fixed-dipole scatterer

a. Born approximation. The results for momentum-transfer cross sections (averaged over orientations) is well defined (finite) for all values of D, for either finite or point-dipole scatterers.[4] The total cross section in the Born approximation is infinite for all D.

b. Exact. Results for the fixed *point* dipole yield a finite momentum-transfer cross section $\bar{\sigma}_m$ for $D < D_c$, but an infinite value for $D > D_c$.[5] For a *finite* dipole $\bar{\sigma}_m$ is defined for all D, but the total cross section is again infinite[7] independent of the magnitude of D or of the dipole length.

B. Dipole rotor scatterer

a. Born approximation. The momentum-transfer and the total cross sections are well behaved for all D.[2,3] In the Born approximation this statement holds for finite and point dipoles. In this approximation the elastic scattering cross section is zero for a pure-dipole scatterer.[2] The rotational excitation and deexcitation cross sections become infinite in the limit as $I \to \infty$.

b. Exact. For a finite rotor the momentum-transfer, the total elastic, and inelastic cross sections are all well behaved for all values of D. Rotational excitation and deexcitation cross sections are generally much larger than the elastic scattering cross section. In the limit as $I \to \infty$ the cross sections for rotational transitions diverge in the exact treatment[7] as they do in the Born approximation. For the point-dipole rotor, as shown above, the momentum-transfer and total scattering cross sections are well defined for $D < 0.639ea_0$, with resonant structures in various partial-wave channels, but both become undefined for $D \geq 0.639ea_0$.

Finally we add, perhaps unnecessarily, that the

unphysical behavior of the solutions to the quantum scattering problems involving simple fixed and freely rotating-point dipole scatterers, does not obviate their usefulness in certain applications to charged-particle scattering by polar molecules. Again there are interesting subtleties in the convenience and accuracy of such applications. It was noted earlier, for example, that in estimating electron momentum-transfer cross sections for polar gases through the use of a simple point-dipole scatterer, the Born approximation gave better agreement with experiment than did the exact result for the same problem.[5] This point was discussed later by Crawford *et al.*[25] To this we may now add a similar comment regarding the calculation of rotational excitation and deexcitation cross sections. That is, higher angular-momentum (large J) contributions to $\sigma(j,j')$ can be conveniently and accurately represented through the Born approximation. Further, the Born results for a *point*-dipole rotor are analytic and converge with increasing J to agreement with exact results for a real molecular target of the same dipole moment and moment of inertia (see the recent review by Collins and Norcross[26]). The interesting twist added herein, is that the exact treatment of scattering by a point-dipole rotor yields a result that is again *poorer* than the Born approximation in describing a real scattering problem. Unlike the Born result, the present study reveals that higher angular-momentum components of the exact solution for the point-dipole rotor do not converge to the identical partial-wave components of the cross sections for scattering by a real molecular target of the same D and I.

The real utility of the solutions for the simple dipole potential occurs in frame transformation treatments of electron scattering by polar molecules,[26,27] where the problem is divided, on the basis of physical arguments, into different regions of configuration space. In this technique use is made of a body frame description of the system at small and intermediate distances from an origin within the molecule where the fixed point-dipole results find application (for higher "partial waves" of the unorthodox functions of Eqs. (7) and (8) where no collapse occurs, and/or in a region which is away from the origin but inside the nonadiabatic asympototic regime[27]). At large distances, where nonadiabatic effects start to play an important role in the description of the problem, a transformation is made to a laboratory frame where analytic Born results for the dipole rotor can be utilized. (Since the Born results are better, the exact solutions for the *point-dipole rotor* will not find useful application in treating scattering by either subcritical or supercritical scatters.) A recent application has been made by Clark and Siegel[28] of the analytic properties of the simple point-dipole problem in their frame transformation treatment of electron scattering by LiF.

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APPENDIX

The equivalence at $r \sim 0$ of the point dipole and the point-dipole rotor problems can be shown as follows. First, the expansion (14) can be written more explicitly as

$$\Psi^{JM}(\vec{r},\hat{D}) = \sum_{jl}\sum_{m_j m_l} (jm_j lm_l | jlJM) Y_j^{m_j}(\hat{D}) Y_l^{m_l}(\hat{r}) U_{jl}^J(r)/r . \tag{A1}$$

The angular functions $Y_l^{m_l}(\hat{r})$ can be expressed in a coordinate system (r,θ',ϕ') which rotates with the dipole rotor (having z' axis along $\hat{D}$). To this end we use the Wigner matrix element $D^{(l)}_{\mu m_l}(\alpha\beta\gamma)$ where $\alpha\beta\gamma$ are the Euler angles between the rotating coordinate system and the space fixed frame. Thus,

$$Y_l^{m_l}(\theta,\phi) = \sum_{\mu} D^{(l)}_{\mu m_l}(\alpha\beta\gamma) Y_l^{\mu}(\theta',\phi') . \tag{A2}$$

With the transformation (A2) we have (A1) in the form[29]

$$\Psi^{JM}(\vec{r},\hat{D}) = \sum_{jl}\sum_{m_j m_l} (jm_j lm_l | jlJM) Y_j^{m_j}(\hat{D}) \sum_{\mu} D^{(l)}_{\mu m_l}(\alpha\beta\gamma) Y_l^{\mu}(\theta',\phi') U_{jl}^J(r)/r . \tag{A3}$$

The transformation of Ψ^{JM} to the rotating coordinate system is completed by expressing $Y_j^{m_j}(\hat{D})$ in the form of a $D^{(j)}_{0m_j}$ function and by coupling the two D matrices as follows:

$$Y_j^{m_j}(\hat{D})D^{(I)}_{\mu m_I}(\alpha\beta\gamma)=\left(\frac{(2J+1)}{4\pi}\right)^{1/2}D^{(j)}_{0m_j}(\beta\gamma)D^{(I)}_{\mu m_I}(\alpha\beta\gamma)$$

$$=\left(\frac{(2j+1)}{4\pi}\right)^{1/2}\sum_K(j0l\mu\,|jlK\mu)(jm_jlm_l\,|jlKm_j+m_l)D^{(K)}_{\mu,m_j+m_l}(\alpha\beta\gamma)\,.$$

From the properties of the vector coupling coefficient we can carry out the sum over m_j and m_l in (A3) (where $m_j+m_l=M$) and write finally

$$\Psi^{JM}=\sum_{jl\mu}\left(\frac{(2j+1)}{4\pi}\right)^{1/2}(j0l\mu\,|jlJ\mu)D^{(J)}_{\mu,M}(\alpha\beta\gamma)Y_l^{\mu}(\theta',\phi')U^J_{jl}(r)/r\,. \tag{A4}$$

In the coordinates (r,θ',ϕ) we note that the potential term $e\vec{D}\cdot\vec{r}/r^3$ of Eq. (11) is simply $eD\cos\theta'/r^2$. Also the functions $D^{(J)}_{\mu,m}$ are eigenfunctions of H_R in Eq. (11) with eigenvalues $J(J+1)\hbar^2/2I$. Finally, we can define a new radial function $F_{l,\mu}(r)$ through the relation

$$F_{l,\mu}(r)=\sum_j\left(\frac{(2j+1)}{4\pi}\right)^{1/2}(j0l\mu\,|jlJ\mu)U^J_{jl}(r) \tag{A5}$$

such that

$$\psi^{JM}=\sum_{l,\mu}D^{(J)}_{\mu,M}(\alpha\beta\gamma)Y_l^{\mu}(\sigma',\phi')F_{l,\mu}(r)/r \tag{A6}$$

and note that near $r=0$ the terms $J(J+1)\hbar^2/2I$ may be neglected in comparison to the r^{-2} terms in the radial equations. With (A6) the Schrödinger equation for the rotating dipole in (r,θ',ϕ') coordinate takes the simple form near the origin

$$\left(\frac{d^2}{dr^2}-\frac{l'(l'+1)}{r^2}\right)F_{l,\mu}(r)\cong\frac{eD}{r^2}\sum_l\langle Y_l^{\mu}(\theta',\phi')\,|\cos\theta' Y_l^{\mu}(\theta',\phi')\rangle F_{l,\mu}(r)\,,$$

where we have omitted the energy terms k_{jj}^2, which are negligible near the origin. This is exactly the form of the Eqs. (10) for the fixed point dipole (near $r=0$ where k^2 can be again omitted). Thus in the limit as $r\to 0$ we may identify the solutions $F_{l,\mu}$ as the radial functions F_{lm} for the point dipole field. Indeed,

$$F_{l\mu}(r)=\sum_j\left(\frac{(2j+1)}{4\pi}\right)^{1/2}(j0l\mu\,|jlJ\mu)U^J_{jl}(r)\Big|_{\lim r\to 0} \tag{A7}$$

Note also that, as shown in Ref. 7, the equations for the dipole rotor become identical to those of the fixed dipole (at all values of r) in the limit as $I\to\infty$, where k^2 and k_{jj}^2, are degenerate.

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[17]W. R. Garrett, Phys. Rev. A 22, 1769 (1980), has shown that the critical moments for a dipole rotor, normally a function of J, I, and of the radial quantum number (number of nodes), become degenerate in the

point-dipole limit. The present result is predictable from that behavior of D_c^J.

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[19]In the electron-dipole rotor problem the solutions also preserve an additional parity quantum number P, which can be defined (Ref. 20) as $(-1)^{j+l-J}$. For electrons scattering from a rotor in the ground state only the even parity solutions are involved. In Ref. 17 the critical moments for these solutions were shown to merge at $D_c = 0.639ea_0$ in the point-dipole limit. By the same argument the odd-parity solutions for the point-dipole rotor critical binding problem converge to $D_c = 3.792ea_0$. Thus if one considers the general scattering problem including scattering from rotationally excited targets, the odd-parity solutions of the present problem become undefined at $D = 3.792ea_0$. This is somewhat immaterial since the general point-dipole scattering problem cannot be defined above $0.639ea_0$.

[20]Since the critical dipole moments associated with higher total angular-momentum states of a finite dipole grow larger with increasing J, it is to be expected that the resonant structures in the partial cross sections, $\sigma^J(j,j')$ for the point-dipole rotor, will shift even closer to D_c with increasing J. Nevertheless, the individual components of σ continue to misbehave in the limit as $D \to D_c$ even in the limit as $J \to \infty$.

[21]The results shown in the figures are not exact in the sense that the boundary condition at the origin was satisfied only through a parametric two-dimensional treatment of the matrix equation for the exponent in the starting condition $U \sim ar^s$. This could affect oscillations very near $D = D_c$, which are on a scale too closely spaced to be shown in the figures.

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