THE THREE-PARTICLE PROBLEM IN ATOMIC PHYSICS

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INTRODUCTION

My main objective today is to give you some notion of the complexities and subtleties of the three-particle problem in atomic physics, with emphasis on recent progress, especially in areas bearing on presently unresolved questions. For the purposes of this paper the particles are structureless and their interactions are purely electrostatic. In other words, I shall be concerned solely with systems of three particles obeying the so-called zero order Hamiltonian, of generic form

$$H_0 = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 - \frac{\hbar^2}{2m_3} \nabla_3^2 + \frac{Z_1 Z_2 e^2}{|r_1 - r_2|} + \frac{Z_2 Z_3 e^2}{|r_2 - r_3|} + \frac{Z_3 Z_4 e^2}{|r_3 - r_4|}.$$ 

Thus this paper will be concerned mainly with those special features of three-particle systems associated with the special characteristics of Coulomb forces. Of course, real atomic three-particle systems are not completely described by the Hamiltonian $H_0$, which ignores corrections stemming from quantum electrodynamic effects, spin-orbit coupling, etc.\(^1\) Such corrections are of very fundamental interest, as has been discussed by various speakers both at this Conference and at the First International Conference on Atomic Physics two years ago.\(^2\) However, these corrections have no bearing on the considerations of this paper.

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There have been numerous recent reviews of our experimental and theoretical knowledge concerning atomic three-particle systems. Indeed, reviews of this sort were given by quite a few speakers at the First Conference two years ago. For this reason I shall not try to give a comprehensive review of the atomic physics three-particle problem in this talk. Instead, I'm going to concentrate on a few specific somewhat diverse topics wherein I feel there have been noteworthy theoretical developments during the past two years or so. My choice of such topics has been neither unique nor exhaustive. Furthermore, the time limitation on this paper precludes as detailed a discussion as the topics I do examine deserve.

Because Coulomb forces are long range, the theory of atomic three-particle collisions -- or of multi-particle collisions for that matter -- involves special complications, but also some possible special simplifications. For example, in the scattering of an electron by a neutral atom the distortion of the atom by the electron cannot be ignored, even when the incident electron is very far from the atom. Correspondingly, customarily relied on mathematical procedures often break down in collisions under Coulomb forces. For instance, scattering matrix elements may fail to converge; incident waves are renormalized. On the other hand, because they are simple in form as well as long range, with Coulomb forces we can hope to achieve normally unattainable mathematical simplifications. In particular, in the three-particle problems governed by the above Hamiltonian $H_0$, one can hope to take advantage of the unusually convenient properties of the solutions to Schrödinger's equation for two-particle Coulombic systems. As a matter of fact, for two-particle systems -- among all reasonably realistic velocity-independent local interactions -- only the Coulomb permits expressing in closed analytic form the eigenvalues and eigenfunctions, bound state and continuum, for all angular momenta. Moreover, the equality of the classical and quantum mechanical cross sections for two-particle Coulomb scattering suggests that atomic three-particle collisions can be treated classically when a single one of the three interactions in $H_0$ is predominantly important, as reasonably might be assumed to be the case in, e.g., the ionizing collisions between fast electrons and hydrogen atoms. Furthermore, because a low energy charged particle in a Coulomb field receives a momentum transfer which is well known to be large compared to the Heisenberg momentum uncertainty, one can also argue that even the ionization of atomic hydrogen by slow electrons should be understandable classically, though of course not on the basis of merely a binary encounter model. Illustrative applications of these remarks concerning the special features of Coulomb forces will be discussed below. It also may be worth mentioning that in low energy $e^-$-He$^+$ scattering (a three-body atomic collision I shall not discuss significantly in this paper) there is a mathematically well-founded quantum mechanical approach based specifically on the fact that the attractive Coulomb potential
has an infinite number of bound states. This approach, the so-called quantum defect method, was described by Seaton at the Conference two years ago.

**ELECTRON-HYDROGEN SCATTERING**

I now turn to the three-particle system $e^- e^+ H^+$ involved in the collisions between electrons and atomic hydrogen. In this system the proton mass can be put equal to infinity, for my purposes, so that the zero order Hamiltonian reduces to

$$H_0 = -\frac{\hbar}{2m_e} \nabla_1^2 - \frac{\hbar}{2m_e} \nabla_2^2 - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{|r_1 - r_2|}.$$  \hspace{1cm} (1)

The Hamiltonian (1) has a theoretically and experimentally well-established bound state, namely the ground state of $H^+$, about 0.7 eV below the atomic hydrogen ground state $H(1s)$. But showing how tricky the atomic three-particle problem can be --- it also is known that if one electron has a mass $m'$ not necessarily equal to the usual electron mass $m_e$, then a three-particle bound state lying below $H(1s)$ does not exist unless $(2/3)m_e < m' < (3/2)m_e$.

If there were no electron-electron interaction (i.e., if the last term in (1) were absent), the $H^+$ system would have an infinite number of stable bound states lying above $H(1s)$; for example, there would be a stable $H^+(2s^2)$ state at an energy 6.8 eV above $H(1s)$. With the inclusion of the $e^2/r_{12}$ term, these electronically doubly excited states of $H^+$ normally are expected to autoionize; in other words, for the actual Hamiltonian (1) these doubly excited states normally are not truly bound, but instead correspond to decaying non-quadratically-integrable continuum states. Theory indicates this existence of infinitely many autoionizing doubly excited states of $H^+$ should be associated with the existence of infinitely many resonances in the elastic scattering of electrons by atomic hydrogen

$$e^- + H(1s) \to e^- + H(1s).$$  \hspace{1cm} (2a)

I shall not describe the detailed theory of the positions and widths of these resonances, which theory was reviewed by Burke at the Conference two years ago. I do want to state that the theory indicates there actually should be an infinite number of elastic scattering resonances at incident electron energies below the threshold for excitation of atomic hydrogen by electrons

$$e^- + H(1s) \to e^- + H(2s), H(2p), H(3s), \text{ etc.}$$  \hspace{1cm} (2b)
The existence of an infinite number of resonances below the H(2s) excitation threshold can be understood on the basis that the H(2s) atom has an infinite polarizability, because of the 2s-2p degeneracy in atomic hydrogen (where I am ignoring relativistic effects, the Lamb shift, etc., as previously stressed). This infinite polarizability causes a breakdown of the usual argument that an electron incident on a neutral atom sees an attractive induced dipole \( r^{-4} \) potential. In actuality, an electron incident on an H(2s) atom sees an attractive \( r^{-2} \) potential, which is sufficiently long range and sufficiently strong to support an infinite number of bound states. Furthermore, the fact that the outgoing electron in the excitation reactions (2b) moves in an attractive long range potential affects the threshold behavior of these excitation cross sections, as Wigner recognized back in 1948. For short range forces [which in this context includes \( r^{-4} \) potentials] the excitation cross section \( \sigma_{ex}(E) \) near the threshold energy \( E_t \) is proportional to the square root of the energy excess

\[
\sigma_{ex}(E) \sim (E-E_t)^{1/2}
\]

(3a)

a result which follows solely from phase space arguments. For the hydrogen excitation reactions (2b), however, detailed analysis shows that the cross sections oscillate in a rather complicated and rapid fashion at energies immediately above threshold, but at threshold have a finite limit, namely

\[
\lim_{E \to E_t} \sigma_{ex}(E) = C_f \neq 0
\]

(3b)

where \( C_f \) depends on the final excitation level, of course.

These immediately preceding assertions about the behavior of the elastic and inelastic \( e^-+H(1s) \) cross sections are contained in Burke's paper of two years ago, at which time it was becoming clear that the theory of \( e^-+H(1s) \) collisions, elastic and inelastic [reactions (2a)-(2b)], is well in hand at energies from 0 to a few volts above the inelastic threshold at 10.2eV. However the data on which this happy conclusion is based were just beginning to come in when Burke spoke two years ago. It now can be concluded that at energies from 0 to about 12eV the shapes of the measured elastic and inelastic cross section curves are in accord with theoretical expectation, and that the magnitudes of the experimental cross sections differ by at most 20% from the close coupling predictions of Burke et al. Certainly it no longer can be maintained that for excitation to the H(2s) state there is a discrepancy of about a factor of two between theory and experiment, as was thought to be the case three years ago.

The close coupling calculations I have been discussing can
be carried out in several ways, including taking advantage of a variational formulation. In essence, however, the close coupling method projects the Schrödinger equation on a finite set of bound states, and then without further approximation solves numerically the resultant set of coupled equations for the projection amplitudes. The aforementioned 20% agreement with experiment in effect was obtained with a so-called six state expansion, in which 1s-2s-2p-3s-3p-3d eigenfunctions are employed; use of merely a simple 1s-2s-2p three state expansion, without additional "correlation terms" or other means of taking into account higher eigenfunctions, is insufficient to yield the 20% agreement between theory and experiment cited above. Actually, the close coupling method—already very arduous at energies below 12eV even with the best modern high speed computers—rapidly becomes impractical in e⁻-H(1s) collisions as the incident energy is increased above 12eV. Moreover, even if one could afford the computer time, at higher energies, where important cross section structure (due, e.g., to resonances) is not expected, the close coupling method seems overly elaborate for the purposes of the theory. In other words, as Burke stressed in his talk two years ago, for e⁻-H(1s) collisions it is important to find a theory which is valid in the intermediate energy range from about the ionization threshold (13.6eV) to 150 or 200eV; above 200eV Born approximation should be good enough to provide at least a practical starting point for accurate cross section predictions.

GLAUBER CALCULATIONS

During the past two years there has been significant progress in developing such an intermediate energy range theory. About fifteen years ago Glauber,12 on the basis of an eikonal-type formulation, obtained closed-form approximate expressions for scattering amplitudes, elastic and inelastic. Since its introduction, the Glauber approximation has been employed extensively in nuclear physics and in fundamental particle physics, but [perhaps because of the increasing parochialism of present-day physics] only very recently13 has the Glauber approximation been employed in atomic physics. Basically the Glauber is a high-energy approximation, if only because it explicitly assumes scattering angles are small. However, it seems much superior to first Born approximation (FBA) (to which it reduces at high energies) in that the Glauber involves all powers of the interaction, not merely the first power as in FBA.

In the case of e⁻-H(1s) collisions, the Glauber approximation to the amplitude $A_{1f}(K_{1f})$ for scattering from initial state $u_i$ to final state $u_f$, with momentum transfer (in units of $\hbar$),
\[ \dot{q} = \dot{k}_1 - \dot{k}_f \]

is

\[ A_{I_f}(k_1^* - k_f^*) = \frac{ik_1}{2\pi} \int d\tilde{r}_2 (d^2 b) u_f^0(\tilde{r}_2) e^{i\dot{q} \cdot \tilde{b} - i\Gamma(\tilde{b}, \tilde{r}_2) \cdot \dot{r}_2} \]  \hspace{1cm} (4)

where \( \tilde{b} \) is the impact parameter vector, in the plane perpendicular to the incident electron velocity \( \dot{v}_1 \),

\[ \Gamma(\tilde{b}, \tilde{r}_2) = 1 - e^{-i\chi(\tilde{b}, \tilde{r}_2)} \]

\[ \chi(\tilde{b}, \tilde{r}_2) = -\frac{1}{\hbar v_1} \int_{-\infty}^{\infty} dz' V(\tilde{b} + z' \frac{\dot{v}_1}{v_1}, \tilde{r}_2) \]

\[ V(\tilde{r}_1, \tilde{r}_2) = -\frac{e^2}{\tilde{r}_1} + \frac{e^2}{|\tilde{r}_1 - \tilde{r}_2|} \]

and we are supposing electron 1 is incident on the initially bound electron 2. The form of Eq. (4), wherein only the initial and final bound state eigenfunctions appear explicitly, shows that in lowest order the Glauber approximation is ignoring precisely what the close coupling approximation emphasizes, namely the coupling to intermediate states during the progress of the collision; in the Glauber formula (4) coupling to intermediate states is implicit rather than explicit, through the powers of the interaction \( V \) appearing when \( e^{i\chi} \) is expanded in a power series.

Because the Coulomb interactions in \( V(\tilde{r}_1, \tilde{r}_2) \) have so simple a form, the formidable-appearing five-dimensional integral (4) can be reduced to a one-dimensional integral without further approximation for \( e^{-\hbar \Pi(1s)} \) elastic scattering or excitation, a feat not normally possible with non-Coulombic interactions. For example, for \( 1s-2s \) excitation, Eq. (4) reduces to

\[ A_{I_f}(k_1^* - k_f^*) \equiv A_{I_f}(q) \]

\[ = \frac{2^{10} i k_1}{3^{6} \sqrt{2}} \int_{0}^{\pi/2} d\theta \sin^{3} \theta \cos \theta \left[ -2 \sin^{4} \theta + \frac{56}{9} \cos^{2} \theta \sin^{2} \theta - \frac{128}{81} \frac{4 \cos^{4} \theta}{\sin^{2} \theta + \frac{4}{9} \cos^{2} \theta} \right]^{5} \]

\[ \times \left\{ 1 - |\cos \theta|^{2n+1} \sum_{\frac{1}{2}}^{\frac{1}{2}} (\frac{1}{2} + \frac{1}{2} \sin 2\theta) \right\} \]  \hspace{1cm} (5)

where \( n = e^{-2}/\hbar v_1 \). The integral (5) is readily and inexpensively evaluated with the aid of a high speed computer.
Figure 1. 1s - 2p excitation cross section in units of $\pi a_0^2$. The triangles are the data points. The curves show various theoretical estimates of 1s - 2p excitation, computed via Glauber and various other approximations discussed in the text.

Figure 1 displays a comparison of the experimental H(1s)-H(2p) excitation cross section with various theoretical estimates, in the energy range from about 15 to 200eV. The triangles are the data points. I don't want to discuss in detail the various theoretical curves of Fig. 1. However, I should state that the Ochkur is a not very well-founded attempt to incorporate an improved estimate of electron exchange into the First Born approximation (FBA); c.c. denotes 1s-2s-2p close coupling calculations (there have been no six state close coupling calculations at these energies). Evidently all the theoretical estimates coincide above about 200eV. Below 200eV the Glauber clearly is superior to all other theoretical estimates except the Vainshtein, which however also appears not very well-founded, in that it involves a number of simplifying assumptions introduced largely for mathematical convenience. The failure of the Glauber at energies below about 30eV is ascribable to a combination of two effects: First, the Glauber, being basically a high energy approximation, necessarily becomes poorer at low energies; second, the Glauber neglects electron exchange, which in this e-H(1s) collision is independently estimated to become important only at energies below 40eV.
Figure 2. Differential cross sections for excitation of the n=2 levels of atomic hydrogen (a) at 100 eV; (b) at 200 eV. The circles (1) are the data points. Curves 2 and 3 are theoretical angular distributions, all normalized to the experimental data points at $\theta = 21^\circ$. Curve 2 (dashed), the Born-Oppenheimer approximation; curve 3 (solid), the Glauber approximation.

Figure 2 illustrates\textsuperscript{14} the ability of the Glauber to predict observed angular distributions; at 200eV the agreement with experiment is almost perfect. The data points are observed angular distributions\textsuperscript{17} of scattered electrons following excitation to the 2s or 2p levels of atomic hydrogen; because the experimental angular distributions were only relative, not absolute, the data have been normalized to the theoretical distributions at a scattering angle $\theta = 21^\circ$. The Born-Oppenheimer approximation is the conventional First Born approximation, but now including the exchange amplitude along with the direct amplitude; there are no close coupling calculations of any kind at the energies of Fig. 2.

**THRESHOLD IONIZATION**

Next I concentrate on the ionization of atomic hydrogen by slow electrons

$$e^- + H(1s) \rightarrow e^- + e^- + H^+$$

(6)
a subject of major present interest to atomic theorists. The question at issue is what is the threshold law for this process, i.e., how does the cross section depend on the energy excess at incident electron energies just above the 13.6eV ionization threshold. If the forces were short range the ionization cross section near threshold would be proportional to the square of the energy excess

$$\sigma_{\text{ion}}(E) \propto (E-E_t)^2$$  \hspace{1cm} (7a)

a result which [like the short range excitation threshold law (3a)] follows solely from phase space arguments. If the electron-electron interaction $e^2/r_{12}$ is ignored in the final state, i.e., if each outgoing electron moves in the pure Coulomb field of the proton fixed at the origin, the threshold law for $e^-\text{H}(1s)$ ionization is altered to

$$\sigma_{\text{ion}}(E) \propto (E-E_t)$$  \hspace{1cm} (7b)

The difference between Eqs. (7a) and (7b) can be understood on the basis that in the long range Coulomb field of the proton the wave function of each electron acquires a renormalization factor proportional to $\nu^{1/2}$, $\nu$ the outgoing electron velocity. If there are reasons to think the wave function of only one of the electrons should be renormalized, then

$$\sigma_{\text{ion}}(E) \propto (E-E_t)^{3/2}$$  \hspace{1cm} (7c)

For example, it has been argued that (7c) should be more nearly correct than (7b) because most of the time the outgoing electrons have different speeds, implying one of the electrons usually sees merely a screened Coulomb field at long range. Moreover, the possibility that the true threshold law is intermediate between (7b) and (7c) cannot be ruled out. Thus Temkin suggests

$$\sigma_{\text{ion}}(E) \propto (E-E_t)^{(3-\gamma)/2}$$  \hspace{1cm} (7d)

where $\gamma$ is a number $0<\gamma<1$, or even

$$\sigma_{\text{ion}}(E) \propto -(E-E_t)^{3/2}\log(E-E_t)$$  \hspace{1cm} (7e)

The existing arguments for any of the threshold laws (7c), (7d), or (7e) hardly are convincing. There are quantum mechanical derivations of (7b) based on more sophisticated arguments than merely dropping the $e^2/r_{12}$ interaction in the final state, but they have not led to general acceptance of the linear form (7b) as the correct threshold law for ionization. In short, at present there is no generally accepted form of the ionization threshold law, nor
is there any generally agreed upon quantum theoretic approach to a derivation of that law. For this reason, recent years have seen an increasing interest in classical derivations of the ionization threshold law. As was explained early in this paper, such interest is not illogical, in view of the special properties of Coulomb forces. In particular, there has been much interest in the threshold law deduced via purely classical orbit arguments by Wannier in 1953, namely

$$\sigma_{ion}(E) \approx (E-E_t)^2 + \sqrt{3}/4 \approx (E-E_t) 1.127$$  \(7f\)

a power law which if there were any justice should be unknown to science, if I may paraphrase the immortal words of a famous chronicler. Justice is rare, however, as we know. At any rate, by the time of Burke's talk two years ago, evidence supporting Wannier's form of the threshold law had just been reported. In particular, McGowan and Clarke concluded that within 0.4eV of threshold the 1.13 power law (7f) is a better fit to the observed e^-H(1s) ionization cross section than either the linear law (7b) or the 3/2 power law (7c). Figure 3 (on next page) shows McGowan and Clarke's analysis of their data within 0.4eV of threshold.

Of course, measurements such as those shown in Fig. 3 never can unequivocally demonstrate a threshold law, because it always can be claimed that the actual threshold dependence is maintained only over a very small energy range, too narrow for observation with presently attainable energy resolution. Still, the assertion that presently available data favor the 1.13 power law over other suggested forms is justified. It probably also is fair to say that theorists seem to be coming round to the belief that Wannier's law is correct. At any rate, very recently there have been several attempts to reach the 1.13 law from a quantum mechanical starting point. In particular, Rau (a student of Fano's) has sought an approximate solution to Schrödinger's equation for the e^-H(1s) ionization problem at near-threshold energies. In the region of configuration space corresponding to Wannier's orbits, Rau finds his solution involves precisely the same strangely irrational quantity \(\sqrt{91/3}\) appearing in the Wannier threshold law (7f); moreover, the energy dependence of Rau's approximate wave functions is precisely as required to yield quantum mechanical e^-H(1s) ionization cross sections varying like \(E_{1,127}\) near threshold.

Rau's analysis, though intriguing and very important, still is far from an inescapable quantum mechanical derivation of Wannier's threshold law, mainly because Rau's approach does not answer the objection that regions of configuration space remote from Wannier's orbits may be important quantum mechanically, though not classically. It must be realized that even if a classical approach can lead to the correct threshold law, Wannier's
Figure 3. The measured ionization cross section for $H(1s)$ near threshold, shown in comparison with various threshold laws $\propto (E-E_T)^n$. The calculated curve for $n=1.00$ represents the data at higher energies but not at threshold. The energy resolution was 0.06eV.

Result could be incorrect; the classical problem of three particles moving under inverse square forces is not solvable analytically, and Wannier has to make subsidiary questionable assumptions (which in some respects Rau adopts). I also remark that Wannier's approach provides a good illustration of a theoretical treatment which takes advantage of the special properties of Coulomb forces, and which could not possibly be successful with short range interactions. Wannier assumes that he can construct classical orbits for electrons which reach infinity with essentially zero energy. To justify this assumption from a quantum mechanical viewpoint, it must be possible to construct wave packets localizing the electrons along Wannier's orbits. At the very least, therefore,
an outgoing electron at some large distance $R$ from the residual ion must have a wavelength $\lambda \ll R$. This requirement cannot be fulfilled for short range forces, wherein an electron reaching infinity with essentially zero energy attains its limiting essentially infinite wavelength at comparatively short distances $R$. Quantitatively, an electron moving in an attractive potential $-V(r)$, and reaching infinity with zero energy, has a wavelength at $R$ given by

$$V(R) = \frac{p^2}{2m} - \frac{\hbar^2}{2m\lambda^2}$$  \hspace{1cm} (8)

or

$$\lambda(R) = \left[ \frac{\hbar^2}{2mV(R)} \right]^{1/2}$$  \hspace{1cm} (9)

For a short range potential, e.g., $V(r) \sim e^{-ar}/r$, Eq. (9) makes

$$\lim_{R \to \infty} \frac{\lambda(R)}{R} = \infty$$  \hspace{1cm} (10a)

On the other hand, for the Coulomb potential $V(r) = e^2/r$, wherein the outgoing electron is being slowed down all the way to infinity, Eq. (9) yields

$$\lim_{R \to \infty} \frac{\lambda(R)}{R} = \lim_{R \to \infty} \left( \frac{\hbar^2}{2me^2} \right)^{1/2} \frac{1}{\sqrt{R}} = 0.$$  \hspace{1cm} (10b)

**FADDEEV EQUATIONS**

In discussions of the three-particle problem these days it is de rigueur to mention the Faddeev equations,\textsuperscript{28} and I am getting too old to flout convention. In three-particle collisions, even with short range forces, the (until recently) unquestioningly employed Lippmann-Schwinger integral equation for the wave function solving Schrödinger's equation has serious mathematical deficiencies.\textsuperscript{28-29} In particular, there is no assuredly convergent iterative solution to the three-particle Lippmann-Schwinger equation, nor—if such an iterative solution did converge—is there any assurance that it would converge to that solution of the Schrödinger equation satisfying the boundary conditions appropriate to the collision being studied. Faddeev's contribution was to derive a set of three coupled integral equations which avoids these deficiencies. More specifically, successive Fredholm approximations to the solution of Faddeev's equations assuredly converge to the wave function satisfying Schrödinger's equation for the correct boundary conditions.

In addition to the desirable property just noted, the Faddeev
three-particle equations have the feature that they explicitly involve the two-particle scattering operators (the so-called T-operators) rather than the two-particle interaction potentials. This feature is physically attractive, but in most circumstances is a complication rather than a help, because it generally is not possible to express the two-particle scattering operators in closed analytic form. For Coulomb interactions, however, the two-particle T-operators can be expressed in analytic form, in terms of hypergeometric functions as a matter of fact. Consequently use of Faddeev's equations in atomic three-particle problems may be practical.

The foregoing assertions concerning the Faddeev equations essentially are contained in Watson's review at the First Conference two years ago. At that time Watson remarked that an application of the Faddeev equations to prediction of the \( e^+ - H(1s) \) elastic scattering resonances had just been completed, by Ball, Chen and Wong.\(^{31} \) Since then, there have been quite a spate of publications on the use of Faddeev's equations in atomic three-particle problems, including \( e^+ - H(1s) \)^{31,32} collisions and the charge transfer collisions of protons with atomic hydrogen,\(^{33,34} \) which in the laboratory system is symbolized by

\[
\text{H}^+ + \text{H}(1s) \rightarrow \text{H}(1s) + \text{H}^+ \tag{11}
\]

incident at rest outgoing at rest

It is fair to conclude from these researches that the Faddeev equations—though deserving further investigation—are by no means a panacea for the intricacies of the atomic three-particle problem. Even though the Coulomb two-particle T-operator is exactly known, the Faddeev equations are too complicated to solve without further approximation. The very recent charge transfer investigations\(^{33,34} \) merely evaluate a first iteration of the Faddeev expression for the T-operator; there is little reason to believe that a non-Fredholm iteration of the Faddeev equations is any more reliable than series iteration of the original Lippmann-Schwinger integral equation. On the other hand, Chen et al.\(^{31,32} \) actually have solved a simplified set of Faddeev equations, obtained by in effect approximating the Coulomb interaction by a finite sum of separable interactions. However, as yet Chen's Faddeev results are not as good as the close coupling results, and have only been carried through for elastic \( e^+ - H(1s) \) collisions; moreover, it appears\(^{35} \) that this procedure of Chen et al.\(^{33,34} \)—though seemingly a very new approach to the problem of predicting atomic collision cross sections—actually is intimately related to the close coupling procedure of approximating the wave function by a projection on a finite set of eigenfunctions. I add that Carpenter and Tuan's results\(^{34} \) do not agree with those of Shastry et al.,\(^{33} \) although both groups supposedly compute the same Faddeev first iteration. The reason for the discrepancy between these two presumably identical Faddeev calculations has not
been elucidated, but very likely is connected with the many mathematical pitfalls encountered in evaluating integrals containing the Coulomb T-operator.

In any event, all these applications of the Faddeev equations to atomic three-particle collisions gloss over the fact that the Faddeev equations were derived originally only for short range forces, under circumstances wherein we could be sure the wave function for purely two-particle collisions obeyed the Lippmann-Schwinger integral equation

$$\psi_1^{(+)} = \psi_1 - \frac{1}{E - i\varepsilon} V \psi_1^{(+)}$$  \hspace{1cm} (12a)$$

For Coulomb interactions V, West\(^1\) has argued that the integral equation actually is homogeneous, namely

$$\psi_1^{(+)} = - \frac{1}{E - i\varepsilon} V \psi_1^{(+)}$$  \hspace{1cm} (12b)$$

If (12b) is correct, the form of the Faddeev equations for particles moving in Coulomb fields surely will be affected. The latest last word on this subject undoubtedly is Faddeev's own; in a recent review Faddeev asserts\(^2\) that his equations in their customary form are valid for e⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⇒ collisions at energies below the ionization threshold, as in the work of Chen et al.,\(^3\) but that his equations may require modification at energies above the ionization threshold, as in the charge transfer calculations.\(^4\)

Irrespective of whether the Faddeev equations are valid in atomic three-particle collisions, there remains the problem of extracting from the wave function (however obtained) predictions which can be compared with the results of experiment. This problem is especially subtle when three or more independently moving bodies are involved in the collision, as e.g., in so-called three-three reactions, wherein three bodies are incident and produce three outgoing products. Such reactions probably are only of theoretical interest in nuclear or particle physics, but they can be important in chemical systems. A typical problem might be to determine the reaction rate for the four particle three-three reaction

$$\{1,2\} + 3 + 4 \rightarrow 1' + 2 + \{3,4\}$$  \hspace{1cm} (13a)$$

under the circumstances that there also can occur the three-particle two-two reactions

$$\{1,2\} + 3 \rightarrow 1 + \{2,3\}$$  \hspace{1cm} (13b)$$
\[(2,3) + 4 \rightarrow 2 + \{3,4\} \quad (13c)\]

where the numbers index the particles, and the braces indicate a bound state. It can be shown that the observed reaction rate for (13a) will not be independent of the volume of the reaction chamber unless the experimentalist somehow eliminates the possibility that (13a) can occur via the sequence (13b)-(13c). Assuming the experimentalist indeed sets up his apparatus to eliminate the sequence (13b)-(13c), one must ask with what theoretical expression shall his observations be compared, recognizing that the wave function describing the collision certainly contains asymptotic portions corresponding not only to the direct three-body reaction (13a), but also to the sequence (13b)-(13c). For three-particle systems the only three-three reaction is elastic scattering

\[1 + 2 + 3 \rightarrow 1 + 2 + 3 \quad (14)\]

and the problem is to compute a volume-independent elastic scattering coefficient. This problem I recently have been able to solve for short-range forces.\textsuperscript{38} Specifically, if the elastic scattering coefficient \(\overline{\nu}\) is to be computed from the usual "Golden Rule"

\[
\overline{\nu} (i-f) = \frac{2\pi}{\hbar} \frac{1}{(2\pi)^6} \langle f | T^t | i \rangle \delta(E_f - E_i) \delta(k_f - k_i) \frac{dk_1}{dk_2} \frac{dk_3}{dk_3} \quad (15a)
\]

* [where the \(\delta\)-functions conserve energy and momentum, and \(dk_1dk_2dk_3\) are the final density of states in a plane wave representation] then \(T^t\) must differ from the usual \(T\)-operator

\[T = V - V \frac{1}{H - E - i\epsilon} V \quad (15b)\]

as indicated diagramatically below.

\[T = \begin{array}{c}
1 \\
2 \\
3 \\
\vdots \\
1 \\
2 \\
3 \\
\vdots
\end{array} + \begin{array}{c}
1 \\
2 \\
3 \\
\vdots
\end{array} + \begin{array}{c}
1 \\
2 \\
3 \\
\vdots
\end{array} + \begin{array}{c}
1 \\
2 \\
3 \\
\vdots
\end{array} + \cdots \quad (16a)\]
where the dots signify the obvious permutations of the preceding diagram, and the bubble denotes a fully completed binary collision

\[ \begin{array}{c}
\begin{array}{cccc}
1 & 1 & 1 & 1 \\
2 & 2 & 2 & 2 \\
3 & 3 & 3 & 3 \\
\end{array}
\end{array}
\quad + \quad
\begin{array}{c}
\begin{array}{c}
\text{intermediate}
\end{array}
\end{array}
\quad + \quad
\begin{array}{c}
\begin{array}{c}
\text{etc.}
\end{array}
\end{array}
\quad = 
\]

On the other hand,

\[ T^t = \]

\[ \begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\text{intermediate}
\end{array}
\end{array}
\end{array}
\quad + \quad
\begin{array}{c}
\begin{array}{c}
\begin{array}{c}
\text{etc.}
\end{array}
\end{array}
\end{array}
\quad = 
\]

where the inequality means that the double-scattering diagram on the right side of \((16c)\) is to be included in \(T^t\) if—and only if—the energy of the intermediate state (at the dashed line) lies off the energy shell. In other words, \(T^t\) is the sum of all contributions from \(n \geq 3\) successive binary collisions, plus the contributions from double-scattering diagrams wherein energy is not conserved in the intermediate state [although of course in these elastic scattering diagrams the initial and final energies are equal after all scatterings have been completed]; if \(T^t\) is allowed to include single-scattering diagrams, or diagrams corresponding to truly physical double scattering (where the intermediate state lies on the energy shell), then the elastic scattering coefficient computed from \((15a)\) will not be volume-independent. The result \((16c)\) for \(T^t\) is not unexpected, but to demonstrate it convincingly requires a fair amount of analysis. What the corresponding expression for \(T^t\) should be in the case of Coulomb forces, or whether it even makes sense to seek a volume-independent elastic scattering coefficient in the Coulomb case, I do not have the slightest idea.
REFERENCES


3. N. F. Mott and H. S. W. Massey, The Theory of Atomic Collisions (Oxford, 1965); B. L. Moiseiwitsch and S. J. Smith, Rev. Mod. Phys. 40, 238 (1968); H. S. W. Massey, E. H. S. Burhop and H. B. Gilbody, Electronic and Ionic Impact Phenomena (Oxford, 1969). These reviews also contain many references to the atomic collision literature. Further references, experimental and theoretical, may be found in various bibliographies issued by the Joint Institute for Laboratory Astrophysics Information Center, University of Colorado, Boulder, Colorado, and by the Atomic and Molecular Processes Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee.


5. That an incident plane wave is renormalized in potential scattering by a pure Coulomb field has been demonstrated by S. Okubo and D. Feldman, Phys. Rev. 117, 292 (1961); see also Robert A. Mapleton, J. Math. Phys. 2, 482 (1961) and 3, 297 (1962).


8. For other useful expositions of this theory along with additional references to the literature, see S. Geltman, Topics in Atomic Collision Theory (Academic Press, New York, 1969), Part II; Massey, Burhop and Gilbody, reference 3, volume 1, chapters 8 and 9.


19. For a particle in an attractive Coulombic potential, the radial wave functions properly normalized at infinity are proportional to $r^{-1/2}$ at finite radial distance $r$, in the limit as $r \to 0$; see Mott and Massey, reference 3, pp. 60-63, esp. Eq. (37b).

The same $r^{-1/2}$ behavior as $r \to 0$ is manifested by the renormalization factor computed by Okubo and Feldman, reference 5, esp. Eq. (56).


because of the aforementioned infinite polarizability
[ giving rise to effectively $r^{-2}$ interaction potentials] of
the hydrogen atom in excited states.

38. E. Gerjuoy, "Configuration Space Three-Body Scattering Theory,"
Europhysics J. Phys. B., Letter to the Editor, to be
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