Quantum Mechanics in Mathematics, Chemistry, and Physics

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PREFACE

This volume grew from a Special Session in Mathematical Physics organized as a part of the 774th Meeting of the American Mathematical Society in Boulder, Colorado, 27-29 March, 1980. The organizers attempted to include a mix of mathematicians, physicists and chemists. As interest in the session increased and as it became clear that a significant number of leading contributors would be here, we were offered the opportunity to have these proceedings published by Plenum Press.

We would like first to express our thanks to Plenum Press, to the American Mathematical Society, and to the University of Colorado Graduate School, and in particular, respectively, to James Busis, Dr. William LeVeque, and Vice Chancellor Milton Lipetz, for their help in this undertaking. We would also like to thank Burt Rashbaum and Martha Troetschel of the Department of Mathematics and Karen Dirks, Donna Falkenhein, Lorraine Volsky, Gwendy Romey, and Leslie Haas of the Joint Institute for Laboratory Astrophysics for their excellent help in the preparation of these proceedings.

The session took on an international character, representing the countries Federal Republic of Germany, India, Belgium, Peoples Republic of China, Switzerland, Iran, Mexico, German Democratic Republic, England, and the United States. In all there were finally 37 speakers and all have contributed to this volume. The success of the meeting is above all due to them.

We chose to mix, rather than separate, the talks and disciplines, in order to promote interaction and appreciation. The contributions are presented here in the same order as they were given at the meeting.

Thus this volume is in some respects an accident, born of a mixing process which began in the pure state of a special session at a regional meeting of a mathematical society and which in its eventual chaos pulled in thirty-seven mathematicians, chemists, and physicists to a final three-day reaction amid a swirling snowstorm that would not stop until the encounter was over.

Boulder, November, 1980
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CONTENTS

TOTAL CROSS SECTIONS IN NON-RELATIVISTIC SCATTERING THEORY

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ABSTRACT

Using time-dependent geometric methods we obtain simple explicit upper bounds for total cross sections σ_{tot} in potential- and multiparticle-scattering. σ_{tot} is finite if the potential decays a bit faster than r^{-2} (in three dimensions) or if weaker direction dependent decay requirements hold. For potentials with support in a ball of radius R bounds are given which depend on R but not on the potential.

We obtain upper bounds on σ_{tot} for large coupling constant λ, the power of λ depending on the falloff of the potential. For spherically symmetric potentials the variable phase method gives also a lower bound growing with the same power of λ.

In the multiparticle case for charged particles interacting with Coulomb forces the effective potential between two neutral clusters decays sufficiently fast to imply finite total cross sections for atom-atom scattering.

We reexamine the definitions of classical and quantum cross sections to discuss some puzzling discrepancies.

1. OUTLINE

The total scattering cross section in quantum mechanics is a simple measure for the strength of a potential when it influences a homogeneous beam of particles with given energy and direction of flight. It can be easily measured in experiments, therefore various approximation schemes have been developed for its calculation. On the other hand relatively little attention has been paid to a mathematically rigorous treatment, probably because it is a rather special quantity derived from basic objects like the scattering amplitude or the scattering operator S. Moreover various assumptions and estimates were motivated by technical rather than physical reasons. In contrast to the conventional time independent approach Amrein and Pearson [1] used time dependent methods to obtain new results. In Amrein, Pearson,and Sinha [2] this was extended to prove finiteness of the total cross section in the multiparticle case if all pairs of particles which lie in different clusters interact with short range forces.

In our approach we add geometric considerations to the previous ones. The main bounds are derived by following the localization of wave packets as they evolve in time. This method is both mathematically simple and physically transparent. Nevertheless it allows to recover or improve most results with simpler proofs. We need not average over directions but we keep the direction of the incident beam fixed. The main defect of the geometric method so far is that we have to average over a small energy range; our bounds blow up in the sharp-energy limit. Consequently we get poor bounds for the low energy behavior or (connected by scaling) for obstacle scattering with the radius going to zero.

In Section 3 we determine the decay requirements for infinitely extended potentials which guarantee finite total cross sections both for the isotropic and anisotropic cases. They are close to optimal. We obtain explicit bounds which have the correct small coupling and high energy behavior. The Kupsch-Sandhas trick is used in the next section to give a bound independent of the potential if the latter has its support inside a ball of radius R. The bound has the correct large R behavior.

One of our main new results combines the two bounds to establish a connection between the decay of the potential at infinity and the rate of increase of the total cross section in the strong coupling limit (Section 5). The variable phase method gives lower bounds with the same rate of increase for spherically symmetric potentials.

The main advantage of time dependent (and geometric) methods is that two cluster scattering is almost as easy to handle as two particle (= potential-) scattering. One has to use a proper effective potential between the clusters which may decay faster than the pair potentials due to cancellations. For a system of charged particles interacting via Coulomb pair potentials the effective potential between neutral clusters (atoms) decays fast enough to give a finite total cross section for atom-atom scattering (including rearrangement collisions and breakup into charged clusters). This new result is derived in Section 7.

In quantum mechanics textbooks usually the classical total cross section is defined first and then the quantum total cross section is derived by analogy. Therefore it is puzzling that both quantities differ considerably even if the quantum corrections should be small. E. g. the quantum cross section is twice as big as the classical one for scattering from big hard spheres ("shadow scattering"), even when $\hbar \to 0$.

In Section 2 we examine the limits involved in the derivation of the quantum total cross section and show that it is basically a pure wave- (and not particle-) concept. This suggests our definition of the quantum total cross section (2.5), which agrees with the traditional one for suitable potentials. (Or one might use (2.5) as an equivalent expression for σ_{tot} which is convenient for estimates.) This point of view explains naturally the discrepancies; we discuss some aspects of the classical limit in Section 6.

For detailed references to earlier and related work see [1,2, 8, 11]. We restrict ourselves here to three dimensions, the results for general dimension as well as various refinements and extensions can be found in [8].

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2. THE DEFINITION OF CLASSICAL AND QUANTUM TOTAL CROSS SECTIONS

When scattering experiments are performed with microscopic particles like atoms, electrons, nuclei, then (in contrast to billard balls) it is practically impossible to observe the time evolution of individual projectiles. We have to restrict ourselves to very few observables which can be measured well enough,

e. g. the direction of flight of the particle when it has passed the target. This direction is asymptotically constant, thus there is enough space and time available to measure it with arbitrary precision. In classical physics where the possibility to prepare particles with a given trajectory is not restricted by basic principles, the scattering angle depends strongly on the impact parameter. If the latter cannot be controlled the next best thing is to use a homogeneous beam of incoming particles and to observe the distribution of the outgoing particles over the scattering angles. This is the *classical differential cross section*. Let the incoming beam consist of particles flying in the direction $\hat{e}$ with momentum p and a given density (= number of particles per unit area orthogonal to $\hat{e}$); then one defines:

$$\sigma_{\text{class}}(p,\hat{e};d\Omega) = \frac{\text{number of particles deflected into } d\Omega}{\text{density of particles}}$$

where $d\Omega$ does not contain $\hat{e}$. Integrating over the outgoing directions yields the *classical total cross section*:

$$\sigma_{\text{tot,class}}(p,\hat{e}) = \int_{S^2} \sigma(p,\hat{e};d\Omega)$$

$$= \frac{\text{number of deflected particles}}{\text{density of particles}}$$

(If one thinks of an experiment running forever one should understand the numerators and denominators per given time interval.) Note that the idealization of a beam of finite density which is homogeneous in the plane perpendicular to the beam direction $\hat{e}$, necessarily involves infinitely many particles for two reasons. First one would need infinitely many particles per unit area, but this is compensated by the denominator in the definition of the cross section. The second infinity is more delicate which comes from the infinite extension of the beam. If the target has finite size (potential of compact support) then only the particles which hit the target can be deflected, the infinitely many particles which miss the target go on into the forward direction $\hat{e}$ and won't be counted. (The infinite extension of the beam allows to specify the beam independent of the size and localization of the target.) Excluding *one single* direction from the observation we have singled out the finitely many particles of interest (for finite density) out of the infinitely many incoming. This prevents us from measuring the total cross section exactly if the incoming beam cannot be prepared with all particles having the same direction. The (idealized) concept of the total cross section requires for its definition that there are beams of incoming particles with a sharp direction. On the other hand it is irrelevant whether beams with sharp energy (or modulus of the momentum p) are available or not. We will use this freedom below.

Quantum mechanical scattering states for potentials vanishing at infinity are known to behave asymptotically like classical wave packets. Therefore it is reasonable to extend the notion of cross sections to quantum mechanics. However, a further limit is involved because there are no states with a sharp direction in the quantum mechanical state space. Let the z-axis be in the beam direction $\hat{e}$, then a sharp direction would mean that $p_x = p_y = 0$. By the uncertainty principle this implies infinite extension of the states in the x-y-directions. Thus the infinite extension of the state perpendicular to $\hat{e}$, which might look unnecessary in the classical case, is forced upon us in quantum scattering. We will have to handle wave functions which are constant in the plane perpendicular to $\hat{e}$, therefore the quantum cross section behaves like a quantity characteristic for classical waves rather than classical particles for any $\hbar > 0$. A classical particle approximation would require a wave packet well concentrated compared to a length typical for the potential. Thus it is no longer mysterious that in the classical limit ($\hbar \to 0$) the quantum cross section need not converge to the classical one (e. g. shadow scattering off hard spheres).

Another peculiarity of the classical cross section is its discontinuity under small changes of the potential. Consider e. g.

$$V_b(x,y,z) = (a+bx)\ \chi_{[-r,r]}(z)\ \chi_{[-R,R]}(x)\ \chi_{[-R,R]}(y)$$

for some parameters a,b,r,R where $r \ll R$. If the beam direction is along the z-axis (near the z-axis) for $b = 0$ the total cross section is zero (tiny) but for any $b \neq 0$ is jumps to $4R^2$ ($\approx 4R^2$). If one could easily count the particles which have been influenced by V(e. g.time delay for $a > 0$) the discontinuity of $\sigma_{tot,class}$ at $b = 0$ would disappear and it would always have the size of the geometric cross section $4R^2$. For such a potential with $b = 0$ the quasiclassical limit $\hbar \to 0$ of the quantum cross section does not converge at all!

Following the above considerations about the quantum cross section as a wave limit we use for its definition "plane wave packets" which are chosen to describe waves with a sharp direction of propagation $\hat{e}$ parallel to the z-axis, but they are normalized wave packets in the longitudinal direction, thus being as close as possible to a Hilbert space vector. For a given direction $\hat{e}$ the plane wave space $h_{\hat{e}}$ is isomorphic to (and henceforth identified with) $L^2(\mathbb{R}, dz)$. The configuration space wave function is

$$g(x,y,z) = g(z) \text{ with } \int |g(z)|^2\, dz = 1. \qquad (2.1)$$

In momentum space we denote by $\tilde{g}(k)$ the one-dimensional Fourier-transform

$$\tilde{g}(k) = (2\pi)^{-1/2} \int dz\, e^{-ikz}\, g(z), \tag{2.2}$$

corresponding to the three-dimensional Fourier transform

$$\hat{g}(\vec{k}) = \tilde{g}(k_z)(2\pi)\,\delta(k_x)\,\delta(k_y). \tag{2.3}$$

Since a beam should hit the target from one side only we assume:

$$\text{supp}\,\tilde{g}(k) \subset (0,\infty), \tag{2.4}$$

which implies in (2.3) $k_z = |\vec{k}| =: k$.

The scattering operator S is the unitary operator which maps incoming states to the scattered outgoing waves, it is close to one on states which are weakly scattered. $(S-1)g$ corresponds to the scattered part of the wave g. The probability to detect a scattered particle is then $\|(S-1)g\|^2$ where the norm is that of the Hilbert space $\mathcal{H} = L^2(\mathbb{R}^3)$. Thus we *define* as the quantum mechanical *total cross section*

$$\int_0^\infty \sigma_{tot}(k,\hat{e})\,|\tilde{g}(k)|^2\,dk = \|(S-1)g\|^2, \tag{2.5}$$

where $g \in h_{\hat{e}}$ with (2.4). We will show below that for a class of potentials with suitable decay properties S-1 extends naturally from an operator on $\mathcal{H}$ to a bounded map from $h_{\hat{e}}$ into $\mathcal{H}$, then the definition makes sense. We average over the energy of the incident beam but keep the direction fixed. (See also the similar construction in [14].) Certainly we have to verify that our definition agrees with the conventional one given below.

Within the time independent theory of scattering for potentials with sufficiently fast decay the solutions of the Lippman Schwinger equation have the asymptotic form

$$\phi(\vec{k},\vec{x}) \sim \exp(i\vec{k}\cdot\vec{x}) + f(k;\hat{x}\leftarrow\hat{k})\,\frac{\exp(i\,k|x|)}{|x|} ,$$

$f(k;\hat{x}\leftarrow\hat{k})$ is the continuous on shell scattering amplitude. Equivalently the kernel of S-1 in momentum space is

$$(S-1)(\vec{k}',\vec{k}) = \frac{i}{2\pi m}\,\delta(k'^2/2m - k^2/2m)\,f(k;\hat{k}'\leftarrow\hat{k})$$

where $\hat{k} = \vec{k}/k$, $k = |\vec{k}|$, etc. Then

$$\sigma_{tot}(k,\hat{e}) = \int d\Omega'\,|f(k;\hat{\omega}'\leftarrow\hat{e})|^2. \tag{2.6}$$

The physical motivation for this choice as given in most textbooks on quantum mechanics uses the "obvious" fact that $\exp(i\,\vec{k}\cdot\vec{x})$ describes an incoming homogeneous beam of particles with momentum k, direction $\hat{k}$ and density one (or $(2\pi)^{3/2}$) particle per unit area, similarly for the outgoing spherical wave.

More careful authors give the following time dependent justification. Let $\phi^{in}(\vec{k})$ be the (square integrable) wave function of a single incoming particle with momentum support well concentrated around a mean value $\vec{q}$. The corresponding outgoing state has a momentum space wave function

$$\phi^{out}(\vec{k}') = (S\,\phi^{in})(\vec{k}') = \int d^3k\ \delta(\vec{k}-\vec{k}')\ \phi^{in}(\vec{k}) + $$

$$+ \frac{i}{2\pi m}\int d^3k\ \delta(k'^2/2m-k^2/2m)\ f(k;\hat{k}'\leftarrow\hat{k})\ \phi^{in}(\vec{k}) . \qquad (2.7)$$

The "scattering into cones" papers [6, 9] show that the asymptotic direction of flight is $\hat{k}$ for the incoming and $\hat{k}'$ for the outgoing state. The first summand in (2.7) is then identified as "not deflected" and for continuous (or not too singular) f's the second term gives the deflected part. Although this splitting is natural it cannot be justified by observations for directions lying in the support of $\phi^{in}(\vec{k})$. Under this assumption the probability $w(\phi^{in})$ that a particle with incoming wave function ϕ^{in} will be deflected, is

$$w(\phi^{in}) = \int d^3k' \left| \frac{i}{2\pi m}\int d^3k\ \delta(k'^2/2m-k^2/2m)\,f(k;\hat{k}'\leftarrow\hat{k})\,\phi^{in}(\vec{k})\right|^2 =$$

$$= \| (S-1)\,\phi^{in} \|^2 .$$

To represent a homogeneous beam one translates the incoming state by a vector $\vec{a}$ in the plane orthogonal to the mean direction $\vec{q}$, $\phi^{in}_{\vec{a}}(\vec{k}) = e^{-i\,\vec{a}\cdot\vec{k}}\phi^{in}(\vec{k})$, and one sums up the contributions for different $\vec{a}$'s. $\int d^2a$ represents a homogeneous beam with particle density one per unit area. The resulting number of deflected particles is then

$$\int d^2a\ w(\phi^{in}_{\vec{a}}) = \sigma_{tot}(\phi^{in}) \qquad (2.8)$$

$$= \int d^3k\,(\hat{k}\cdot\hat{q})^{-1} \int d\Omega' |f(k;\hat{\omega}'\leftarrow\hat{k})|^2\ |\phi^{in}(\vec{k})|^2 .$$

In the limit $|\phi^{in}(\vec{k})|^2 \to \delta(\vec{k}-\vec{q})$ expression (2.6) for $\sigma_{tot}(q,\hat{q})$ is recovered and $|\phi^{in}(\vec{k})|^2 \to \delta(k_\perp)|\tilde{g}(k)|^2$ yields $\int dk\ \sigma_{tot}(k;\hat{e})|\tilde{g}(k)|^2$, the left hand side of (2.5). Note that the summation over $\vec{a}$'s is incoherent, we have added probabilities and not states, because we are interested only in interactions between the target and single particles, interference between particles in the beam has to be eliminated.

Let us now calculate the cross section according to our definition.

$$\|(S-1)g\|^2 = \int d^3k' \left| \frac{i}{2\pi m} \int d^3k \ \delta(k'^2/2m-k^2/2m) \right.$$

$$\left. f(k;\hat{k}'\leftarrow\hat{k})(2\pi)\delta(k_\perp)\tilde{g}(k) \right|^2$$

$$= \int dk \int d\Omega' |f(k;\hat{\omega}'\leftarrow\hat{e})|^2 |\tilde{g}(k)|^2 .$$

Thus our definition coincides with the conventional one if the scattering amplitude is continuous (or not too singular).

At first glance it seems strange that the incoherent superposition in (2.8) yields the same result as the coherent superposition of wave packets with strong correlations which forms the plane wave-packets. The following heuristic argument easily explains the phenomenon. Since $(S-1)g \in L^2(\mathbb{R}^3)$ the action of S-1 "localizes", it essentially annihilates the parts of the state which lie beyond some radius r. Let $R \gg r$ and use in the incoherent case (2.8) the normalized wave function

$$g(z) \ (2R)^{-1} \ \chi_{[-R,R]}(x) \ \chi_{[-R,R]}(y)$$

whose (3-dimensional) Fourier transform $\phi^{in}(\vec{k})$ obeys $|\phi^{in}(\vec{k})|^2 \to |\tilde{g}(k)|^2 \ \delta(k_\perp)$ as $R \to \infty$ ($\tilde{g}$ is the 1-dim. Fourier transform). Then

$$w(\phi^{in}_{\vec{a}}) = \|(S-1)\phi^{in}_{\vec{a}}\|^2 \approx \begin{cases} (2R)^{-2} \ \|(S-1)g\|^2 & \text{for } |a_{1,2}| \leq R \\ 0 & \text{otherwise} \end{cases}$$

and

$$\int d^2a \ w(\phi^{in}_{\vec{a}}) \approx \int_{-R}^{R} da_1 \int_{-R}^{R} da_2 \ \|(S-1)\phi^{in}_{\vec{a}}\|^2 \approx \|(S-1)g\|^2 .$$

The sharp direction - limit forces us to use states which are eventually constant in an area much larger than the localization region of S-1. Up to negligible boundary terms all contributions become parallel and the properly normalized coherent and incoherent superpositions do not differ.

In Section 6 we will return to the comparison of the wave picture and particle picture when we discuss the classical limit. There we will explain why it is natural, although it looks unnatural, that the quantum cross section of a hard sphere is twice the corresponding one for classical particles ("shadow scattering"). In the same section we will explain why classical cross sections are generally infinite for potentials with unbounded support although the quantum cross sections may be finite.

3. THE BASIC ESTIMATE FOR σ_{tot}

We assume in this section that the potential $V(\vec{x})$ is a perturbation of the kinetic energy $H_o = -\frac{1}{2}\Delta$ with H_o-bound smaller than 1 (we have set $\hbar=1$ and the particle mass m=1, therefore momenta and velocities coincide). If the potential is of short range (we will impose stronger decay requirements shortly) then the isometric wave operators

$$\Omega^{\mp} = s - \lim_{t\to\pm\infty} e^{i\,Ht}\, e^{-i\,H_o t}$$

exist and are complete, the S-operator

$$S = (\Omega^{-})^{*}\,\Omega^{+}$$

is unitary and on states in the domain of H_o the following "interaction picture" representation holds:

$$S-1 = (\Omega^{-})^{*}\,[\Omega^{+} - \Omega^{-}]$$

$$= (\Omega^{-})^{*} \int_{-\infty}^{\infty} dt\; e^{i\,Ht}\,(iV)\,e^{-i\,H_o t}. \tag{3.1}$$

Cook's estimate gives

$$\|(S-1)\Phi\| \le \int_{-\infty}^{\infty} dt\, \|V\, e^{-i\,H_o t}\Phi\| \;. \tag{3.2}$$

Let $\Phi_R \in \mathcal{H} = L^2(\mathbb{R}^3)$ be an approximating sequence of states which tends to the plane wave packet g as $R \to \infty$. For a suitable class of potentials we will show that

$$\lim_{R\to\infty}\ \sup_{R'>R} \int_{-\infty}^{\infty} dt\, \|V\, e^{-i\,H_o t}(\Phi_{R'} - \Phi_R)\| = 0 \tag{3.3}$$

which implies by (3.2) convergence in $\mathcal{H}$ of $\lim_{R\to\infty}(S-1)\Phi_R =: (S-1)g$ and the finite bound

$$\|(S-1)g\| \le \int_{-\infty}^{\infty} dt\, \|V\, e^{-i\,H_o t} g\| \;. \tag{3.4}$$