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# Quantum Theory of $(H,H_2)$ Scattering: Approximate Treatments of Reactive Scattering*,**



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## DISCLAIMER

## Abstract

A quantum mechanical study is made of reactive scattering in the (H, $H_2$) system. The problem is formulated in terms of a form of the distorted-wave Born approximation (DWBA) suitable for collisions in which all particles have finite mass. For certain incident energies, differential and total cross sections, as well as other attributes of the reactive collisions, (e.g. reaction configuration) are determined. Two limiting models in the DWBA formulation are compared; in one, the molecule is unperturbed by the incoming atom and in the other, the molecule adiabatically follows the incoming atom. For thermal incident energies and semi-empirical interaction potential employed, the adiabatic model seems to be more appropriate. Since the DWBA method is too complicated for a general study of the (H, $H_2$) reaction, a much simpler approximation method, the "linear model" is developed. This model is very different in concept from treatments in which the three atoms are constrained to move on a line throughout the collision. The present model includes the full three-dimensional aspect of the collision and it is only the evaluation of the transition matrix element itself that is simplified. It is found that the linear model, when appropriately normalized, gives results in good agreement with that of the DWBA method. By application of this model, the energy dependence, rotational state of dependence and other properties of the total and differential reaction cross sections are determined. These results of the quantum mechanical treatment are compared with the classical calculation for the same potential surface. The most important result is that, in agreement with the classical treatment, the differential cross sections are strongly backward peaked at low energies and shifts in the forward direction as the energy increases. Finally, the implications of the present calculations for a theory of chemical kinetics are discussed.

# I. INTRODUCTION

The rearrangement scattering of hydrogen atoms by hydrogen molecules ($H+H_2 \rightarrow H_2+H$) is the simplest kind of gas phase exchange reaction. It is of fundamental importance, therefore, for the development of a theory of chemical kinetics.[1,2] From the exact quantum-mechanical solution, we would be able to answer every question concerning this reaction. Unfortunately, an exact treatment is not possible at present, since the reaction involves the motion of six particles, three nuclei and three electrons. After the Born-Oppenheimer separation[3] of nuclear and electronic motion is made, we are still left with a three-body problem involving a complicated potential. While many approximate studies exist,[4-10] their accuracy is not sufficient to answer the basic questions concerning the importance of quantum corrections in chemical kinetics.

To clarify the chemical problem it is useful to consider its relation to nuclear and electron scattering. In nuclear physics, the scattering data are used primarily to investigate the nature of nuclear forces. Hence, one usually assumes certain simple forms for the potential and often treats it as an adjustable quantity by the introduction of suitable parameters. In chemical kinetics, the questions are reversed; that is, from a given potential, it is necessary to determine the reaction cross sections. Although simplified phenomenological potentials have been introduced, the true interaction potential is known to be a complicated function of the interparticle coordinates and to contain important non-additive contributions. Furthermore, methods like the Born and the impulse approximations, which give useful results in high energy nuclear collisions, are not sufficiently accurate in the energy range of chemical interest. In low energy nuclear scattering, the short range of nuclear

forces can be used to advantage; only s- and p-waves need to be considered and cross sections can be correlated with the scattering length. In molecular collisions, by contrast, much longer range forces are involved and a large number of partial waves contribute to cross sections; this holds true even at energies near the threshold of the reaction. Electron scattering from a hydrogen atom[11] is a three-body problem that has greater similarity to chemical reactions. Considerable progress has been made there, in part because the Coulomb interaction between the particles is well defined and has a relatively simple form, so that the entire potential is expressible as a sum of two-body terms. The reactive scattering of the $(H,H_2)$ system suffers in comparison to the electron-hydrogen scattering in that the potential is much more complicated and that there is no scattering center of infinite mass. The latter point is very important because the separable coordinate system suitable for describing the initial state is not the same as that suitable for describing the reacted state. Consequently, a coordinate transformation is required that renders the problem difficult to manipulate analytically. In many nuclear problems (e.g., stripping) this complication is avoided by the assumption that the target is infinitely heavy. However, in three-body collisions between light nuclei (e.g., neutron-deuteron reaction), the same coordinate problem is present. It is, of course, for these nuclear problems that the least progress has been made.[12]

An alternative to the quantum-mechanical approach to chemical reactions is to assume that classical mechanics is valid and to carry out an exact determination of collision trajectories.[13] The cross sections and reaction rates obtained by this method appear to be in general agreement

with the data for the $(H,H_2)$ system. However, the validity of classical mechanics needs to be established. In the absence of a simple criterion for the validity of classical mechanics, the ultimate justification for its use must come from a comparison of a quantum-mechanical calculation with the classical results. If only an approximate solution to the quantum-mechanical problem is possible, the comparison is of particular importance since both the validity of classical mechanics and the approximations in quantum mechanics are subjected to test. For the $(H,H_2)$ reaction system, this type of study especially important because the available experimental results are not completely unequivocal. Furthermore, there is interest in the dependence of the reaction cross section on the internal energy of the reactant and the product molecules. As these energy levels are a quantum-mechanical concept, they have to be incorporated artificially into classical mechanics. Since both the rotational and vibrational energy levels in $H_2$ are widely spaced, the adequacy of the classical approach is doubtful. Finally, it has been held by many that quantum-mechanical tunnelling may often be an important factor in the determination of reaction rates.[1,14] A study of the reactive scattering of $H+H_2$ is especially suitable for a discussion of tunnelling since quantum effects are expected to be more pronounced than in most other systems.

The present work is an approximate quantum-mechanical study of the three-body dynamics in the $(H,H_2)$ system with a realistic, though not exact, potential energy surface[15,16] which has already been used in accurate classical calculations.

## II. FORMULATION

The energies of primary chemical interest for the $(H,H_2)$ scattering correspond to the thermal range below one electron volt. At such low energies, the nuclear velocities are sufficiently small relative to those of the electrons that the Born-Oppenheimer approximation is valid.[3,17] A further simplification for this reaction is that electronic motion can be treated as adiabatic.[1] With these assumptions the scattering process is reduced to the problem of three structureless atoms (with nuclear spin) moving on a potential energy surface that is a parametric function of the relative nuclear distances. The semi-empirical potential energy surface adopted for the present work is complicated by the fact that it includes a large three-body contribution.[15] To facilitate calculation, effective two-body interaction potentials have been constructed by introducing assumptions corresponding to limiting cases of physical interest.[16] In one, the molecule is unperturbed by the incoming atom, and in the other, the molecule adiabatically follows the incoming atom. Although these two limits yield similar results for elastic scattering,[16] the reactive cross sections are found to be very different.

A system of three particles requires nine coordinates to specify the wave function. Since the linear momentum of the center of mass of the system is a constant of motion, three coordinates describing the motion of the center of mass can be separated. Thus, the total wave function can be written as a product of two parts; the first is the eigenfunction of a particle moving in free space, which is simply a plane wave, and the second, involving the remaining six coordinates, is the wave function describing the internal motion relative to the center of mass.

In what follows, we assume that the trivial plane wave part has been separated and are concerned only with the internal motion. Since the total angular momentum of the system is also a constant of motion, three additional coordinates describing the rotation of the system as a whole can, in principle, also be separated.[18] This has been done in some formulations of the three-body problem.[19] However, since the equations resulting from such a separation are time consuming to solve, it is not evident that the evaluation of the complete multi-dimensional integral required for the cross section calculation may not be simpler to do as in certain approximations. The latter procedure, as described below, was followed in the present paper.

To consider the rearrangement scattering A+BC→AB+C, we can write the total system Hamiltonian H in terms of the quantities of the entrance channel α (initial system)

$$H = H_\alpha(\vec{R},\vec{r}) + V_\alpha(\vec{R},\vec{r}), \tag{1}$$

or of the exit channel β (rearranged system)

$$H = H_\beta(\vec{S},\vec{s}) + V_\beta(\vec{S},\vec{s}), \tag{2}$$

where $\vec{R}$ is the coordinate of A relative to the center of mass of BC and $\vec{r}$ is the internal coordinate of BC; $\vec{S}$ is the coordinate of C relative to the center of mass of AB and $\vec{s}$ is the internal coordinate of AB (Fig. 1). The operators $H_\alpha$ and $H_\beta$ are the non-interacting Hamiltonians,

$$H_\alpha(\vec{R},\vec{r}) = -\frac{\hbar^2}{2\mu_{A,BC}}\nabla_R^2 - \frac{\hbar^2}{2\mu_{BC}}\nabla_r^2 + V_{BC}(r), \tag{3}$$

$$H_\beta(\vec{S},\vec{s}) = -\frac{\hbar^2}{2\mu_{C,AB}}\nabla_S^2 - \frac{\hbar^2}{2\mu_{AB}}\nabla_r^2 + V_{AB}(s), \tag{4}$$

where $V_{BC}$ and $V_{AB}$ are the isolated molecular potential of BC and AB, respectively, and the $\mu$'s are the appropriate reduced masses. The terms $V_\alpha$ and $V_\beta$ are initial and final state interaction potentials; that is, $V_\alpha$ is the part of the complete three-body potential $V_T$ that goes to zero as $R\to\infty$ and $V_\beta$ is correspondingly defined for the final channel. Thus,

$$V_T(\vec{R},\vec{r}) = V_T(\vec{S},\vec{s}) = V_{BC}(r) + V_\alpha(\vec{R},\vec{r}) = V_{AB}(s)+V_\beta(\vec{S},\vec{s}) \tag{5}$$

The plane wave solutions of $H_\alpha$ and $H_\beta$ with total energy E are $\Phi_\alpha$ and $\Phi_\beta$, respectively (normalized to unit density),

$$\Phi_\alpha^n(\vec{R},\vec{r}) = \exp(i\vec{k}_\alpha^n\cdot\vec{R})\eta_\alpha^n(\vec{r}), \tag{6}$$

$$\Phi_\beta^m(\vec{S},\vec{s}) = \exp(i\vec{k}_\beta^m\cdot\vec{S})\eta_\beta^m(\vec{s}), \tag{7}$$

where $\eta_\alpha^n$ and $\eta_\beta^m$ are the bound state rotation-vibration eigenfunctions of molecule BC and AB, respectively; that is,

$$\left[-\frac{\hbar^2}{2\mu_{BC}}\nabla_r^2 + V_{BC}(r)\right]\eta_\alpha^n(\vec{r}) = \varepsilon_\alpha^n\eta_\alpha^n(\vec{r}), \tag{8}$$

$$\left[-\frac{\hbar^2}{2\mu_{AB}}\nabla_s^2 + V_{AB}(s)\right]\eta_\beta^m(\vec{s}) = \varepsilon_\beta^m\eta_\beta^m(\vec{s}), \tag{9}$$

where the superscripts n and m represent the quantum number of the initial and final molecular state, and $\varepsilon_\alpha^n$ and $\varepsilon_\beta^m$ are the bound state rotation-vibration eigen energies of molecule BC and AB, respectively. Conservation of energy requires

$$E = \frac{\hbar^2}{2\mu_{A,BC}}(k_\alpha^n)^2 + \varepsilon_\alpha^n = \frac{\hbar^2}{2\mu_{C,AB}}(k_\beta^m)^2 + \varepsilon_\beta^m \tag{10}$$

For the total Hamiltonian H, the initial channel eigenfunctions $\Psi^{(\pm)}_{\alpha,n}$ with energy E and outgoing (+) or incoming (-) spherical wave boundary conditions satisfy the Lippmann-Schwinger equations,[21]

$$\Psi^{(\pm)}_{\alpha,n} = \Phi^{n}_{\alpha} + \frac{1}{E-H_{\alpha}\pm i\varepsilon} V_{\alpha}\Psi^{(\pm)}_{\alpha,n} \tag{11a}$$

$$= \Phi^{n}_{\alpha} + \frac{1}{E-H\pm i\varepsilon} V_{\alpha}\Phi^{n}_{\alpha}; \tag{11b}$$

the positive infinitesimal $\varepsilon$ introduces the appropriate asymptotic behavior. The final channel eigenfunctions $\Psi^{(\pm)}_{\beta,m}$ obey corresponding equations.

In terms of these functions, the differential scattering cross section for rearrangement from the entrance channel $(\alpha,n)$ to the exit channel $(\beta,m)$ can be written[20]

$$\sigma^{mn}_{\beta\alpha}(\vec{k}^{m}_{\beta}) = \frac{\mu_{A,BC}\mu_{C,AB}}{(2\pi\hbar^2)^2} \frac{k^{m}_{\beta}}{k^{n}_{\alpha}} \left| T^{mn}_{\beta\alpha} \right|^2 \tag{12}$$

where $T_{\beta\alpha}$ is the transition matrix (T matrix) defined as

$$T^{mn}_{\beta\alpha} = \langle\Phi^{m}_{\beta}|V_{\beta}|\Psi^{(+)}_{\alpha,n}\rangle = \langle\Psi^{(-)}_{\beta,m}|V_{\alpha}|\Phi^{n}_{\alpha}\rangle \tag{13}$$

Although the transition amplitude in Eq. (13) is exact, it is only a formal expression unless total wave function $\Psi^{(+)}_{\alpha,n}$ or $\Psi^{(-)}_{\beta,m}$ is known. Since its exact evaluation, which is equivalent to solving the three-body Schrödinger equation with appropriate boundary condition, is not feasible at present, approximations have to be introduced to proceed with the cross section evaluation. In most cases, the only approximation method that can

be applied with relative ease is to replace the total wave function $\Psi^{(+)}_{\alpha,n}$ or $\Psi^{(-)}_{\beta,m}$ by the plane wave $\Phi_\alpha$ or $\Phi_\beta$, respectively; that is,

$$T^{mn}_{\beta\alpha} \cong T^{mn}_{\beta\alpha}(B) = \langle \Phi^m_\beta | V_\beta | \Phi^n_\alpha \rangle \quad (14)$$

which is the well-known first Born approximation. Although it may be useful for some atomic rearrangement problems (e.g., high energy, low activation barrier), $T_{\beta\alpha}(B)$ is expected not to give accurate results for the $H+H_2$ reaction in the thermal region.[4,5] This is a consequence of the strong interaction between the atom and the molecule, which distorts the incident wave appreciably, so that the actual wave function differs considerably from a plane wave. In particular, potential leading to reaction is large just in the region where the incident wave can hardly penetrate. If the major effect of the distorting potential can be taken into account, the accuracy of the approximate scattering amplitudes will be greatly improved. This can be done by separating the interaction potential into two parts. One part, which depends only on the distance between the atom and the center of mass of the molecule, modifies the incoming plane wave and is thus responsible for the elastic scattering. The other part, which contains the rest of the potential, is responsible for the processes of excitation and reaction. If one wants to take the principle of detailed balance into account, one must preserve the symmetry between the initial and final states.[22] This means that not only the wave functions of entrance channel but also these of the product channel must be distorted to adjust to the distorting potential.

It is convenient to write

$$V_\alpha(\vec{R},\vec{r}) = V_\alpha^o(R) + V_\alpha'(\vec{R},\vec{r}) \tag{15}$$

$$V_\beta(\vec{S},\vec{s}) = V_\beta^o(S) + V_\beta'(\vec{S},\vec{s}) \tag{16}$$

where $V_\alpha^o(R)$ and $V_\beta^o(S)$ are chosen to account for the strong repulsive interaction between the approaching or receding atom and molecule, subject to the condition that the solutions $\chi_\alpha^{(\pm)}$ and $\chi_\beta^{(\pm)}$ of the Hamiltonians $H_\alpha+V_\alpha^o$ and $H_\beta+V_\beta^o$ can be evaluated exactly or, at least, to a high degree of approximation. The functions $\chi_\beta^{(\pm)}$ satisfy the integral equation, analogous to Eq. (11),

$$\chi_{\beta,m}^{(\pm)} = \Phi_\beta^m + \frac{1}{E-H_\beta \pm i\varepsilon} V_\beta^o \chi_{\beta,m}^{(\pm)} \tag{17a}$$

$$= \Phi_\beta^m + \frac{1}{E-(H_\beta+V_\beta^o)\pm i\varepsilon} V_\beta^o \Phi_\beta^m, \tag{17b}$$

the $\chi_\alpha^{(\pm)}$ satisfy a corresponding equation.

To simplify the writing in what follows, we drop the super or subscripts m and n, except in places where confusion might arise from their omission. It is understood that, when used in connection with a wave function, $\beta$ refers to the final state in the exit channel $(\beta,m)$ and $\alpha$ refers to the initial state in the entrance channel $(\alpha,n)$.

Rewriting the transition matrix $T_{\beta\alpha}$ [Eq. (13)] in the form

$$T_{\beta\alpha} = \langle\Phi_\beta|V_\beta^o|\Psi_\alpha^{(+)}\rangle + \langle\Phi_\beta|V_\beta'|\Psi_\alpha^{(+)}\rangle \tag{18}$$

and using Eq. (17b) to relate $\Phi_\beta$ by $\chi_\beta^{(-)}$ in the second term, we have

$$T_{\beta\alpha} = \langle\Phi_\beta|V_\beta^o|\psi_\alpha^{(+)}\rangle + \langle\chi_\beta^{(-)}|V_\beta'|\psi_\alpha^{(+)}\rangle$$

$$- \left\langle \frac{1}{E-(H_\beta+V_\beta^o)-i\varepsilon} V_\beta^o\Phi_\beta|V_\beta'|\psi_\alpha^{(+)}\right\rangle \qquad (19)$$

$$= \langle\Phi_\beta|V_\beta^o|\psi_\alpha^{(+)}\rangle + \langle\chi_\beta^{(-)}|V_\beta'|\psi_\alpha^{(+)}\rangle$$

$$- \langle\Phi_\beta|V_\beta^o \frac{1}{E-(H_\beta+V_\beta^o)+i\varepsilon} V_\beta'|\psi_\alpha^{(+)}\rangle.$$

The last term of Eq. (19) can be combined with the first term to give

$$T_{\beta\alpha} = \langle\Phi_\beta|V_\beta^o \left(1 - \frac{1}{E-(H_\beta+V_\beta^o)+i\varepsilon}\right) V_\beta'|\psi_\alpha^{(+)}\rangle + \qquad (20)$$

$$\langle\chi_\beta^{(-)}|V_\beta'|\psi_\alpha^{(+)}\rangle.$$

The first term on the right-hand side of Eq. (20) can be transformed

$$\langle\Phi_\beta|V_\beta^o \left(1 - \frac{1}{E-(H_\beta+V_\beta^o)+i\varepsilon} V_\beta'\right)|\psi_\alpha^{(+)}\rangle$$

$$= \langle\Phi_\beta|V_\beta^o \frac{1}{E-(H_\beta+V_\beta^o)+i\varepsilon} (E-H_\beta-V_\beta^o+i\varepsilon-V_\beta')|\psi_\alpha^{(+)}\rangle$$

$$= \langle\Phi_\beta|V_\beta^o \frac{1}{E-(H_\beta+V_\beta^o)+i\varepsilon} (E-H+i\varepsilon)|\psi_\alpha^{(+)}\rangle$$

$$= \left\langle \frac{1}{E-(H_\beta+V_\beta^o)-i\varepsilon} V_\beta^o \Phi_\beta \right| (E-H+i\varepsilon) \left| \Psi_\alpha^{(+)} \right\rangle$$

$$= \langle (\chi_\beta^{(-)} - \Phi_\beta) | (E-H+i\varepsilon) | \Psi_\alpha^{(+)} \rangle . \qquad (21)$$

Since $\Psi_\alpha^{(+)}$ is an eigenfunction of the total Hamiltonian H with energy E, it is evident that as $\varepsilon$ goes to zero this term will vanish. This is well known in the case that the scattering center is infinitely heavy.[23] Here we have explicitly demonstrated that this is also true for collisions in which all particles have finite mass. Thus, we are left with the single term

$$T_{\beta\alpha} = \langle \chi_\beta^{(-)} | V_\beta' | \Psi_\alpha^{(+)} \rangle . \qquad (22)$$

Equations (13) and (22) for the transition matrix are both exact. However, it must be emphasized that they are necessarily equal only if the total wave function $\Psi_\alpha^{(+)}$ used in evaluating $T_{\beta\alpha}$ is exact. In practice, $\Psi_\alpha^{(+)}$ inevitably has to be approximated and the two expressions can give significantly different results. Equation (22) guarantees that the transition matrix is zero when there is no interaction other than that between the particle under consideration and the center-of-mass of the remaining system, but in the formulation of Eq. (13), it vanishes only when the approximation of the total wave function is carried to infinite order.[24] This suggests that Eq. (22) is a better starting point for approximation.

To further simplify Eq. (22), we make use of the relation[25]

$$\Psi_\alpha^{(+)} = \chi_\alpha^{(+)} + \frac{1}{E-H+i\varepsilon} V_\alpha' \chi_\alpha^{(+)} \qquad (23)$$

which follows from the defining integral equations for $\Psi_\alpha^{(+)}$ and $\chi_\alpha^{(+)}$. Substituting into Eq. (22) we obtain

$$T_{\beta\alpha} = \langle \chi_\beta^{(-)} \; V'_\beta [1 + \frac{1}{E-H+i\varepsilon} \; V'_\alpha] | \chi_\alpha^{(+)} \rangle, \tag{24}$$

which is still exact. If the second term on the right-hand side is neglected, Eq. (24) reduces to the distorted wave Born approximation (DWB)

$$T_{\beta\alpha} \cong T_{\beta\alpha}(\mathrm{DWB}) = \langle \chi_\beta^{(-)} | V'_\beta | \chi_\alpha^{(+)} \rangle. \tag{25}$$

The calculations of reactive cross sections presented in this paper are based on Eq. (25).

## III. METHOD OF CALCULATION

It is clear that the accuracy of the DWB calculation depends on how we approximate our total wave function by a judicious choice of $V_\alpha^o$ and $V_\beta^o$. The construction of these two-body potentials and the corresponding wave functions have been described in detail in a previous paper.[16] The spherical symmetric potential is designated as $V_u^o$ when the molecule is unperturbed by the incoming atom;

$$V_\alpha = V_{\alpha u}^o(R) + V'_{\alpha u}(\vec{R},\vec{r}) \tag{26a}$$

$$V_\beta = V_{\beta u}^o(S) + V'_{\beta u}(\vec{S},\vec{s}) \tag{26b}$$

and as $V_a^o$ when the molecule adiabatically follows the incoming atom,

$$V_\alpha = V_{\alpha a}^o(R) + V'_{\alpha a}(\vec{R},\vec{r}) \tag{27a}$$

$$V_\beta = V_{\beta a}^o(S) + V'_{\beta a}(\vec{S},\vec{s}) . \tag{27b}$$

(a) Distorted Wave Born Approximation

To determine the transition amplitude in terms of distorted wave Born approximation (DWB), we need to evaluate Eq. (25). We outline the method for the J=0 and J'=0 exchange reaction of the three-body system, where J refers to the angular momentum of the initial molecule and J' to that of the product molecule. Although the higher transitions require somewhat more complicated formulae, the essence of the method can be brought out by discussion of the simplest transition.

If the molecule is unperturbed by the incoming atom, the wave function is approximated as

$$\chi_\alpha^{(+)}(\vec{R},\vec{r}) \simeq F(\vec{R})\eta_\alpha(r) \tag{28}$$

where $\eta_\alpha(r)$ is the initial molecular wave function in the absence of the incoming atom and $F(\vec{R})$ is the wave function for scattering by the central potential $V_{\alpha u}^{o}(R)$. If the molecule adiabatically follows the incoming atom, the wave function is then approximated as

$$\chi_\alpha^{(+)}(\vec{R},\vec{r}) \cong G(\vec{R})\eta_\alpha(\vec{R},\vec{r}) \tag{29}$$

where $\eta_\alpha(\vec{R},\vec{r})$ is the perturbed molecular wave function[16] which reduces to $\eta_\alpha(\vec{r})$ as $R\to\infty$ and $G(\vec{R})$ is the wave function for scattering by the adiabatic potential $V_{\alpha a}^{o}(R)$. Both $F(\vec{R})$ and $G(\vec{R})$ can be written in the standard partial wave form

$$F(\vec{R}) = \sum_{n=0}^{\infty} (2n+1)i^n e^{i\delta_n} L_n(R)P_n(\cos\theta) \tag{30}$$

and

$$G(\vec{R}) = \sum_{n=0}^{\infty} (2n+1)i^n e^{i\delta'_n} L'_n(R)P_n(\cos\theta) \tag{31}$$

where $\theta$ is the angle between R and the initial wave vector $\underline{k}_\alpha$, and the phase shifts $\delta_n$ and the radial wave functions $L_n$ are obtained from the radial part of the Schrödinger equation with potential $V^o_{\alpha u}(R)$, and $\delta'_n$ and $L'_n$ from that with potential $V^o_{\alpha a}(R)$; the function $L_n(R)$ is the solution bounded at the origin and so normalized as to have asymptotic form[16]

$$L_n(R) \sim \frac{1}{k_\alpha R} \sin(k_\alpha R - \frac{1}{2} n\pi + \delta_n); \tag{32}$$

the function $L'_n(R)$ has the corresponding behavior as $R \to 0$ and $\to \infty$. For $\chi^{(-)}_\beta$ we use the approximate function

$$\chi^{(-)}_\beta(\vec{S},\vec{s}) = H(\vec{S})\eta_\beta(s) \tag{33}$$

where $\eta_\beta(s)$ is the final molecular wave function in the absence of the outgoing atom and $H(\vec{S})$ is the wave function for scattering by the central potential $V^o_{\beta u}(S)$. We use Eq. (33) with $\chi^{(+)}_\alpha$ obtained from Eqs. (26) and (27) to retain the simple form given in Eq. (25) for $T_{\beta\alpha}$. For the adiabatic distortion potential, this introduces an additional approximation into the treatment, which could be avoided by using an alternative, somewhat more complicated, expression for $T_{\beta\alpha}(DWB)$.[19] The function $H(\vec{S})$ can be written in the standard partial wave form[25]

$$H(\vec{S}) = \sum_\ell (2\ell+1) i^\ell e^{i\delta_\ell} L_\ell(S) P_\ell[\cos(\pi-\theta')] \tag{34}$$

where $\theta'$ is the angle between $\vec{S}$ and the final wave vector $\underline{k}_\beta$, and $L_\ell(S)$ is the solution of the Schrödinger equation with the potential $V^o_{\beta u}(S)$, subject to the condition that $L_\ell(S)$ is bounded at the origin and behaves asymptotically as

$$L_\ell(S) \sim (k_\beta S)^{-1}\sin(k_\beta S - \tfrac{1}{2}\ell\pi+\delta_\ell) \tag{35}$$

Substitution of Eqs. (28) or (29) and (33) into the expression for the transition matrix $T_{\beta\alpha}(DWB)$ yields the desired formula. To illustrate the procedure involved, we consider the unperturbed case [Eq. (28)]

$$T_{\beta\alpha}(DWB) = -\int\int\{\sum_{\ell=0}^{\infty}(2\ell+1)i^\ell e^{i\delta_\ell}L_\ell(S)P_\ell[\cos(\pi-\theta')]\}(\eta_\beta(s)) \tag{36}$$
$$\cdot V'_{\beta u}(\vec{S},\vec{s})\cdot\{\sum_{n=0}^{\infty}(2n+1)i^n e^{i\delta_n}L_n(R)P_n(\cos\theta)\}\eta_\alpha(r)d\vec{s}d\vec{S}.$$

It is convenient to choose the volume element of this six-dimensional integral to be

$$d\vec{s}d\vec{S} = s^2\sin\zeta S^2\sin\bar{\theta}d\zeta d\chi d\bar{\theta}d\bar{\phi}dsdS \tag{37}$$

where $\bar{\theta}$ and $\bar{\phi}$ are the angular coordinates of $\vec{S}$, $\zeta$ is the angle between $\vec{s}$ and $\vec{S}$ and $\chi$ is the azimuthal angle of $\vec{s}$ with respect to $\vec{S}$ (see Fig. 1). To perform the integration, we must express the angle $\theta'$ and the coordinates $\vec{R}$ and $\vec{r}$ in terms of the six variables in Eq. (37). With some algebraic manipulation, it can be shown that for $H_3$ system (in which the center-of-mass of each diatomic molecule is at its midpoint)

$$r = [S^2 + \tfrac{1}{4}s^2 + Ss\cos\zeta]^{\frac{1}{2}}$$
$$R = [\tfrac{1}{4}S^2 + \tfrac{9}{16}s^2 - \tfrac{3}{4}Ss\cos\zeta]^{\frac{1}{2}} \tag{38}$$
$$\cos\gamma = (\tfrac{1}{2}r^2 - Ss\cos\zeta - \tfrac{1}{2}s^2)/Rr$$
$$\cos\theta = (\tfrac{1}{2}S\cos\bar{\theta} - \tfrac{3}{2}s(\cos\bar{\theta}\cos\zeta - \sin\bar{\theta}\sin\zeta\sin\chi))/R.$$

Making use of the relation between $\theta'$ and $\bar{\theta},\Theta$

$$\cos\theta' = \cos\Theta\cos\bar{\theta} + \sin\Theta\sin\bar{\theta}\cos(\Phi - \bar{\phi})$$

where $\Theta$ and $\Phi$ are the polar angles of $\underline{k}_\beta$, and of the addition theorem for Legendre polynomials[27]

$$P_\ell(\cos\theta') = P_\ell(\cos\Theta)P_\ell(\cos\bar{\theta}) + 2\sum_{m=1}^{\infty}(-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(\cos\Theta) \tag{39}$$
$$P_\ell^m(\cos\bar{\theta}) \cdot \cos m(\Phi - \bar{\phi}).$$

We see that the $\bar{\phi}$ integration can be done immediately since the integrand depends on it only through Eq. (39). This is expected because the problem is symmetric about the z axis. Substitution of Eq. (39) into Eq. (36) and performance of the $\bar{\phi}$ integration permit the scattering amplitude to be expressed as a series of five-dimensional integrals

$$T_{\beta\alpha}(\mathrm{DWB}) = \sum_{\ell=0}^{\infty}(2\ell+1)A_\ell P_\ell(\cos\Theta) \tag{40}$$

with the partial wave amplitude $A_\ell$ given by

$$A_\ell = \int_0^\infty\int_0^\infty\int_0^\pi\int_0^\pi\int_0^{2\pi} I(\vec{S},\vec{s})\eta_\alpha(r)s^2\sin\zeta S^2\sin\bar{\theta}\,d\chi\,d\zeta\,d\bar{\theta}\,ds\,dS \tag{41}$$

where

$$I(\vec{S},\vec{s}) = -2\pi\exp(-\ell\pi/2 + i\delta_\ell)L_\ell(S)P_\ell(\cos\bar{\theta})(\eta_\beta(s)) \tag{42}$$
$$\cdot V'_{\beta u}(\vec{S},\vec{s})\sum_{n=0}^{\infty}[(2n+1)i^n\exp(i\delta_n)L_n(R)P_n(\cos\theta)]$$

Equation (40) has a form that is similar to that obtained in direct scattering, though the amplitude integral [Eq. (41)] is much more complicated. It should be noted also that the sum in Eq. (40) is over final channel partial waves, which for the present case is equivalent to the expansion over initial channel partial waves.

The differential cross sections are obtained by introducing Eq. (40) into Eq. (12). Integration over the solid angle $d\Omega = \sin\theta d\theta d\Phi$ yields the total cross section

$$\sigma_{\beta\alpha} = 4\pi \frac{\mu_{A,BC}\mu_{C,AB}}{(2\pi\hbar^2)^2} \frac{k_\beta}{k_\alpha} \sum_{\ell=0}^{\infty} (2\ell+1)|A_\ell|^2 \qquad (43)$$

From the perturbed molecular approximation [Eq. (29)] the same formulae are obtained except that the scattering potential $V_u^o$ is replaced by $V_a^o$ and $\eta_\alpha(r)$ and $V_u'(\vec{S},\vec{s})$ are replaced by $\eta_\alpha(\vec{R},\vec{r})$ and $V_a'(\vec{S},\vec{s})$, respectively.

(b) Linear Approximation

Although determination of the $T_{\beta\alpha}(DWB)$ matrix elements outlined in the previous section is possible, the required integral evaluation is so time consuming that only a small number of such calculations were carried out. To permit a more general exploration of the nature of the reaction cross section, it is desirable to use a simpler, but approximately valid, model. The simplifying assumption that we introduce here is that the reaction occurs only in the neighborhood of the linear configuration. Since the potential is minimum for the linear configuration,[15] the initial molecule tends to turn toward the incoming atom. Moreover, the results of the complete DWB approximation calculation show (see Sec. IV) that

the configurations contributing to reaction subtend a cone which is only about 10 percent of the total sphere.

The matrix element $T_{\beta\alpha}$ in this approximation is given by

$$T_{\beta\alpha}(\text{DWBL}) = \Lambda\langle\chi_\beta^{(-)}|V'_\beta\delta(\zeta-\pi)|\chi_\alpha^{(+)}\rangle \tag{44}$$

where $\Lambda$ is the $\delta$-function "strength" parameter. Although $\Lambda$ would be expected to vary as a function of the energy and of the initial and final states, a fixed value of $\Lambda$ was chosen by comparison with a single $T_{\beta\alpha}(\text{DWB})$ result. Because of the arbitrariness in $\Lambda$, all of the work with the DWBL model was based on the simpler unperturbed molecular approximation for the distorted waves associated with the relative motion.

To write out the explicit expression for the matrix element appearing in Eq. (44), we make use of Eq. (36). The linear assumption consists of replacing the surface element $\sin\zeta d\zeta d\chi$ by $\Lambda\delta(\zeta-\pi)d\zeta$. If the initial molecule is in its ground state characterized by the vibration-rotation quantum number (0,0) and the final rearranged molecule is in the $(0,\ell)$th vibration-rotation state, we have

$$\eta_\alpha(\vec{r}) = \phi_o^o(r)$$

$$\eta_\beta(\vec{s}) = \phi_o^k(s)P_k^m(\cos\theta_1)e^{im\phi_1},$$

where $\phi_o^k$ is the radial part of the diatomic molecule wave function, and $P_k^m$ is the (km) associated Lengendre polynomial with $\theta_1,\phi_1$ the polar angles of the molecule. Substituting into Eq. (36), we obtain

$$T_{\beta\alpha}(DWBL) = -\Lambda \iiiint \Big[ \sum_{\ell=0}^{\infty} (2\ell+1) i^{\ell} e^{i\delta_{\ell}} L_{\ell}(S)(-1)^{\ell} P_{\ell}(\cos\theta')$$

$$(\phi_o^k(s) P_k^m(\cos\theta_1) e^{-im\phi_1}) V_u'(\vec{S},\vec{s}) \cdot \Big[ \sum_{n=0}^{\infty} (2n+1) i^n e^{i\delta_n} L_n(R)$$

$$P_n(\cos\bar{\theta})\Big] \cdot \phi_o^o(r)\delta(\zeta-\pi) \cdot S^2 s^2 \sin\bar{\theta}\, d\zeta\, d\bar{\theta}\, d\bar{\phi}\, dS\, ds. \qquad (45)$$

If we expand $P_{\ell}(\cos\theta')$ according to Eq. (39), there are $(2\ell+1)$ terms in the expansion. However, since $\delta(\zeta-\pi)$ is equilvalent to $\delta(\theta_1+\bar{\theta}-\pi)\delta(\phi_1-\bar{\phi}-\pi)$, the $\bar{\phi}$ integration makes all of the terms vanish except the one which has the same m value as the final state of the molecule. To illustrate the calculation with Eq. (45), we write down the expression for the reaction between the ground rotational state of the initial molecule and the k=1, m=0 rotational state of the final molecule. For this case, after the $\zeta$ and $\bar{\phi}$ integrations, we find

$$T_{\beta\alpha}(DWBL) = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-i\frac{\ell\pi}{2} + i\delta_{\ell}} B_{\ell} P_{\ell}(\cos\Theta) \qquad (46)$$

where

$$B_{\ell} = -2\pi\Lambda \int_o^{\infty}\int_o^{\infty}\int_o^{\pi} L_{\ell}(S) P_{\ell}(\cos\bar{\theta}) P_1(\cos\bar{\theta}) \cdot \phi_o^1(s)\; V_u'(\vec{S},\vec{s})$$

$$\cdot \Big\{ \sum_{n=0}^{\infty} (2n+1) i^n e^{i\delta_n} L_n(R) P_n(\cos\bar{\theta}) \Big\} \cdot \phi_o^o(r) s^2 S^2 \sin\bar{\theta}\, d\bar{\theta}\, dS\, ds \qquad (47)$$

with $r = S - \frac{1}{2}s$ and $R = \frac{1}{2}S + \frac{3}{4}s$. To reduce this integral further, we make use of the following relation[28]

$$P_i^m(x) P_j^n(x) = \sum_{k=|i-j|}^{i+j} D(k,i,m,j,n) P_k^{|m-n|}(x). \qquad (48)$$

The nonvanishing D have the form

$$D(k,i,m_1,j,m_2) = (-1)^{g+\ell+m'}(2k+1)\frac{(k-|m_1-m_2|)!}{(k+|m_1-m_2|)!}$$

$$\times \frac{g!(2g-2\ell')!(\ell'-m')!(\ell+m)!}{(g-\ell)!(g-\ell')!(g-\ell'')!(2g+1)(\ell-m)!} \tag{49}$$

$$\times \sum_t (-1)^t \frac{t(\ell''+m''+t)!(\ell+1'-m''-t)'}{(\ell''-m''-t)!(\ell'-m'-t)!(\ell-\ell'+m'+t)!t!}$$

where $i,j > 0$; $g = \frac{1}{2}(i+j+k)$ and an integer, and $|i-j| \leq k \leq |i+j|$. The quantities m", m', m are such that m" is the largest of the triplet, $|m_1|$, $|m_2|$, and $|m_1-m_2|$, m' is the next largest and m is the smallest; and $\ell''$,$\ell'$ and $\ell$ are the corresponding members of the triplet i, j, k; the sum over t is to be taken over all terms involving non-negative factorials. Substituting from Eq. (48) into Eq. (47) and performing the $\bar{\theta}$ integration, we obtain

$$B_\ell = -\frac{4\pi\Lambda}{2\ell+1} \sum_{j=|\ell-1|}^{\ell+1} (2j+1)D(\ell,j,o,1,o)i^j e^{i\delta_j} b_{\ell j} \tag{50}$$

where

$$b_{\ell j} = \int_o^\infty \int_o^\infty L_\ell(S)\phi_o^1(s)V_u'(S,s)L_j(R)\phi_o^o(r)s^2S^2 dsdS \tag{51}$$

Thus, the evaluation of $T_{\beta\alpha}$(DWBL) has been reduced to a sum over the two-dimensional integrals $b_{\ell j}$. Corresponding expressions result for molecules in other initial and final states.

## IV. CALCULATIONS AND RESULTS

Numerical evaluations of the partial wave amplitudes and cross sections have been carried out by means of computer programs, which are described briefly in the Appendix. Here we report some of the results obtained for the $H+H_2$ reaction with the initial and final molecule in the ground vibrational state. The initial rotational state of the reactant molecule is denoted as J and the final state of the product molecule by J'. We consider first the DWB approximation and then turn to the more extensive studies by the DWBL model.

### (a) Distorted Wave Born Approximation

Both the unperturbed molecule and the adiabatic molecule approximation were used. Some total cross sections obtained as a function of energy for the J=0 to J'=0 reaction with the two limiting approximations are shown in Table 1. The first incoming energy (0.5eV) is well above the classical threshold (.25eV)[13] energy; the second one (0.33eV) is near the classical threshold energy and the third one (0.21eV) is well below the classical threshold. As can be seen from the table, the adiabatic model yields a total cross section which is about twenty times larger than that of the undistorted model. From the magnitude of the rotational coupling and the associated characteristic times, we believe that the adiabatic model is a considerably better approximation for the energies under consideration.

The differential cross section (in arbitrary units) obtained from the adiabatic model at an energy of 0.5eV is shown by the solid line in Fig. 2. It corresponds predominantly to "backward scattering" in the center-of-mass system; that is, the incoming atom strikes the molecule,

and a new molecule is formed which goes back mainly in the direction from which the atom came. The differential cross section obtained for the undistorted molecule model is very similar in shape to that from the adiabatic model, although the magnitude is, of course, much smaller.

From Eq. (40), it is evident that $|A_\ell|^2$ represents the contribution of the $\ell$-th partial wave to the total cross section. A plot of $|A_\ell|^2$ against $\ell$ is given in Fig. 3 for energy of 0.5eV. The relationship between $|A_\ell|^2$ and $\ell$ corresponds to that between the reaction probability and the impact parameter in the classical picture. It is found that $|A_\ell|^2$ decreases smoothly with increasing $\ell$ and approaches zero for $\ell \simeq 10$. Thus, the magnitude of $|A_\ell|^2$ as a function of $\ell$ provides information on the size of the reactive region.

In order to obtain some idea of the configurations of the three nuclei that lead to reaction, we use the unperturbed molecule model and consider a quantity $T_{\beta\alpha}(DWB,\tau)$ defined as

$$T_{\beta\alpha}(DWB,\tau) = \langle \chi_\beta^{(-)} | V'H(\tau-\zeta) | \chi_\alpha^{(+)} \rangle \tag{51}$$

where $H(x)$ is the Heaviside function [$H(x) = 0$, $x<0$; $H(x) = 1$, $x>0$] and $0 \leqslant \tau \leqslant \pi$; thus, $T_{\beta\alpha}(DWB,\pi) = T_{\beta\alpha}(DWB)$. From Eqs.(40) and (51),

$$T_{\beta\alpha}(DWB,\tau) = \sum_{\ell=0}^{\infty} (2\ell+1) A_\ell(\tau) P_\ell(\cos\Theta) \tag{52}$$

where

$$A_\ell(\tau) = \iiiint I(\gamma,\tau)\eta_\alpha(\vec{r})s^2S^2 \sin\zeta \sin\bar{\theta}\, d\chi\, d\zeta\, d\bar{\theta}\, ds\, dS. \tag{53}$$

The function $I(\gamma,\tau)$ is defined by

$$I(\gamma,\tau) = \begin{cases} 0 & \text{when } \gamma > \tau \\ I(\vec{S},\vec{s}) & \text{when } \gamma \leqslant \tau \end{cases} \tag{54}$$

with $I(\vec{S},\vec{s})$ given in Eq. (42); the angle $\gamma$ depends on the five integration variables through Eq. (38). The total cross section $\sigma_{\alpha\beta}(\tau)$, which is obtained from Eq. (43) by $|A_\ell|^2$ replacing $|A_\ell(\tau)|^2$, provides a semclassical measure of the contribution to reaction for atom, molecule orientations with $\gamma$ in the range between 0 and $\tau$. The quantity $\sigma_{\alpha\beta}(\tau)/\sigma_{\alpha\beta}$ for the J=0 to J'=0 reaction at an initial energy of 0.5eV is plotted as a function of $\tau$ in Fig. 4. The figure demonstrates that the dominant contribution to the reaction cross section comes from small-angle configurations; i.e., 80% of the cross section is obtained with $\gamma \leqslant 40°$. These results coupled with the fact that the molecule turns toward the incoming atom[16] suggest that the linear model should be a satisfactory approximation.

(b) Linear Approximation

For the linear calculation, the $\delta$-function strength parameter was chosen so that the total cross section obtained by this method at incident energy of 0.5eV is the same as the value obtained from the complete distorted wave Born approximation. The differential cross section at an incident energy of 0.5eV for the reactions J=0 to J'=0,1,2 (summed over all possible m values) are presented in Fig. 5. In all cases, the initial and final molecule are in the ground vibrational state. We see that the

various curves are similar, with a strong backward peak being the dominant feature. Since the complete distorted wave Born approximation treatment had a corresponding form for the J=0 to J'=0 case (solid line in Fig. 2), the comparison provides additional evidence for the validity of the linear model. Moreover, it should be clear that the present linear model is very different in concept from treatments in which the three atoms are constrained to move on a line throughout the collision; such an approach, of which the accurate $H+H_2$ calculation of Truhlar-Kuppermann[29] is a recent example, provides only reaction probabilities and does not permit the evaluation of differential cross sections. In the present linear approximation, the full three-dimensional aspect of the collision is included and it is only the evaluation of the transition matrix element itself that is simplified.

The shape of the differential cross section as a function of incident energy for the J=0 to J'=0 reaction is shown in Fig. 6. As the incident energy increases, the peak in the cross section gradually shifts in the forward direction. This type of behavior, in which the incoming atom "remembers" where it came from as its energy becomes considerably larger than the barrier energy is familiar from nuclear physics. For the (d,p) stripping reaction in a Coulomb field, the differential cross section is peaked backward for an incident energy of a few MeV[30] but the peak is drastically shifted toward the forward direction[31] when the energy is increased to a few hundred MeV. In the atom-molecule case, the shift in the peak direction occurs over an energy range on the order of 2eV. It would be extremely interesting to have data on the energy

dependence of the differential cross section for a better understanding of the reaction mechanism.

The energy dependence of the total cross section for J=0 to J'=0,1,2 reactions is shown in Figs. 7 and 8. The solid triangles are the values obtained by the distorted wave Born approximation for the J=0 to J'=0 case. Since the presently available reaction rate data emphasize the low-energy range ($E \leq 0.6$eV), an expanded plot is given in Fig. 7, while the more general energy dependence is shown in Fig. 8. The dominant feature of the curves for all J' is the steep increase in $\sigma$ with incident energy, up to a maximum at about 0.8 to 0.9eV, and a subsequent drop off for higher energies. It is expected that the reaction cross section will continue to decrease as the incident energy is increased; further, for very high energies, the process $H+H_2 \rightarrow 3H$ becomes important. For all of the energies studied (except in the neighborhood of the threshold), it can be seen that the J=0 to J'=1 reaction has the largest cross section, J=0 to J'=2 is next, and that the J=0 to J'=0 actually has the lowest cross section. However, quantitatively the difference between the various cross sections is not great, being less than a factor of two over the entire energy range. The threshold results with J=0 to J'=0 becoming largest are reasonably understood in terms of the available energy.

## V. DISCUSSION

In this section we compare the results of the quantum treatment with the classical calculation for the same potential surface, consider some alternative approximations for a quantum-mechanical approach to reactive scattering, and comment on some of the implications of the present calculations for a theory of chemical kinetics.

### (a) Comparison with Classical Theory

Although the question of whether classical mechanics is adequate for chemical reaction rate calculations is a fundamental one, no unequivocal answer is available. Since a detailed classical treatment exists for the $(H,H_2)$ reaction,[13] we hope to provide some information on this point by comparing the present quantum results with the classical ones. The fact that the classical and the quantum calculation used the identical potential energy surface makes the agreement or disagreement particularly significant, independent of the availability of experimental data. However, it should be noted that differences between the classical and the quantum results could be due to the approximations in the present treatment, as well as to "real" quantum effects.

The most important result is that the differential cross sections obtained from the classical calculation is almost identical in form with that from the quantum-mechanical calculation (see Fig. 2). Both are highly anisotropic with a broad backward peak and essentially no scattering for $\theta<90°$.

For a relative translational energy of 0.5eV where the most extensive classical and quantum-mechanical calculations were done, the total quantum-

mechanical cross section is less than the classical cross section by about a factor of two. The comparison is not completely unequivocal since in the quantum-mechanical treatment, only the transition from J=0 to J'=0 was calculated by the distorted wave Born approximation, while the other transitions were estimated by linear model approximation. At lower energies, the linear quantum model gives results that drop more rapidly to zero than the classic values, while at higher energies the quantum cross section rises rapidly above the classical result. The high-energy quantum values suffer from the breakdown of the adiabatic approximates which would require a variation in the strength parameter in the linear approximation. Also, the linear model is expected from classical calculations[13] to be less accurate at higher energies. Finally, the DWB method itself becomes less valid as the magnitude of the total cross section increases. Thus, significance of the comparison of the energy dependence between the classical and quantum calculations is somewhat uncertain. However, a possible explanation for the larger cross section obtained in the classical calculation in the low-energy range is the zero-point molecular vibration (equal to the quantum-mechanical zero-point energy) incorporated into the classical calculation. More of this energy may be available for crossing the barrier in the classical than in the quantum treatment. Also, the equilibrium distance of the molecule is the most probable place for the two atoms in quantum mechanics. However, in classical mechanics, vibrational motion makes the two atoms spend most of the time at the extremal positions. Since it has been found that reaction occurs most easily when the molecule is stretched to its extreme length, a larger classical cross section is not unexpected.

The above comparison suggests that the quantum and classical results are similar in many, though not all, respects. This is somewhat surprising since the choice of the $(H,H_2)$ was suggested by the fact that, since it is the lightest element, it has the longest de Broglie wavelength for a given energy. Thus, many authors have suggested that quantum effects should be very pronounced for the $(H,H_2)$ system. Considering a one-dimensional barrier approximation for a reaction, Kondratev[32] gives a condition for the validity of the classical limit as

$$(\hbar F/\mu^2 v^3) \ll 1 \tag{54}$$

where F is the effective force ($F = -d\mathcal{V}/dx$ where $\mathcal{V}$ is the potential and x is the distance), $\mu$ is the mass and v is the velocity of the particle. Since for a hydrogen atom, hydrogen molecule collision at 300°K, the most probable velocity gives $(\hbar F/\mu^2 v^3) \approx 15$, it may be concluded that classical mechanics is not applicable. Also, Mazur and Rubin[33] in a a quantum-mechanical calculation for a linear system with an idealized potential found that the reaction rate computed by solving the Schrödinger equation differed by at least a factor of 5 from the classical value. More recently, Mortensen[10] studied the $(H,H_2)$ system with the atoms constrained to move on a line and found that there is a large discrepancy between classical and quantum results.

We must consider why there are no significant quantum effects in certain features of the $(H,H_2)$ reaction when the condition for the validity of classical mechanics appears to be violated, as discussed in the introduction of this section. One point is that the condition

established for one-dimensional motion may not be correct for the three-dimensional case. Also, it is likely that the linear calculations which constrain the atoms to move on a line show larger quantum effects than the complete three-dimensional calculation in which the greater number of degrees of freedom may lead to some blurring of quantum effects. Finally, the particles with energies that violate the validity condition [Eq. (54)] have a very small reactive cross section and do not contribute to the general behavior. For example, at 300°K, most of the particles do not react at all; only the collisions corresponding to the high-energy tail of the distribution make an important contribution to the cross section and those satisfy the condition; e.g., for an incident energy of 0.5eV, $\hbar F/\mu^2 v^3 \cong 10^{-2}$. It should also be mentioned that the recent exact calculations[34] of idealized linear collisions show that for certain potential barrier the quantum and classical results agree well with each other.

(b) Alternative Approximations

The distorted wave Born approximation is obtained when we replace $\Psi_\alpha^{(+)}$ by the elastically scattered wave $\chi_\alpha^{(+)}$ in Eq. (22). The results reported in the paper were based on this approximation. If the substitution of $\Psi_\alpha^{(+)}$ by $\chi_\alpha^{(+)}$ were made in Eq. (13), we obtain an alternative approximation. The results of that approximation have the general features of the distorted wave Born approximation except that the differential cross section has a sharp forward peak in addition to the broad backward peak. Although the forward peak might be thought to be due to the diffraction effect of wave mechanics, an examination of the polar intensity of the incoming particle near the reactive region shows that this interpretation is incorrect. The forward peak is spurious and is caused by the use of an

inconsistent approximation; that is, the distortion of both the initial and the final wave is required in calculating the transition amplitude. This conclusion is in accord with the principle of detailed balancing.

A calculation with the Born transition amplitude [Eq. (14)] yielded a differential cross section that oscillates violently as a function of angle and is large in the forward direction. This result confirms the inapplicability of Born approximation to a process in which the repulsive distortion of the wave function is very important.

The distorted wave Born approximation has been successfully applied to a large class of nuclear scattering problems.[35] In these treatments, the usual approach has been to utilize a potential that includes some adjustable parameters. Thus, it is not always certain whether the agreement with experiment justifies the method or whether errors in the method are compensated by the suitable altered potential. In the present calculation, the potential used was completely independent of the scattering data and no adjustable parameter was introduced. Thus, the comparison with the classical and the experimental results is of greater significance. It appears from the present results that the distorted wave Born approximation is a valid first step in the study of chemical reactions with activation energy; that is, many reaction attributes (e.g., form of differential cross section) are obtained with sufficient accuracy with this approximation. However, for some properties (e.g., energy dependence of the total cross section) a more detailed treatment is required. In particular, although the adiabatic approximation used here is probably satisfactory for the vibrational degree of freedom of the molecule, it may be less appropriate for rotation. To examine this

question, a coupled equation approach is now being employed for the study of the $H,H_2$ reaction.[36]

(c) Implications for Chemical Kinetics

In absolute rate theory,[2] the reaction is assumed to proceed through some intermediate region whose properties can be formulated in terms of an "activated complex." It is assumed that collisions in which the reactive system passes through this region can be characterized by assuming that there is an equilibrium phase space distribution among the degrees of freedom of the "activated complex." Some difficulties with this assumption in the purely classical treatment have been described previously.[37] For the quantum-mechanical problem, there is the added complication that the time spent in the transition region determines the widths of the "energy levels" of the activated complex, so that, if the complex "lifetime" is too short, a simple evaluation of its partition function may not be valid.

In the present calculation we assume that, given the potential surface, the dynamical problem can be solved in sufficient detail to obtain the reaction attributes from first principles. A direct interaction approach is used and no intermediate state is introduced into the theory. From a complete set of scattering cross section and their energy dependence, the macroscopic rate coefficient and its temperature dependence can be determined[38] in a simple fashion for comparison with the kinetic measurements. With the classical cross sections, such a rate constant calculation has been made and surprisingly good agreement with the measured values was obtained.[13] The results of the quantum-mechanical treatment

that were obtained here are too limited to permit a corresponding rate constant evaluation.

From the classical treatment and its comparison with the quantum-mechanical calculation, there is no evidence for an "activated complex" with an extended lifetime. Thus, quantization of certain of the degrees of freedom (e.g., the bending vibrations) may not occur in this reaction. However, a number of the concepts associated with usual chemical reaction rate theory are supported by the quantum-mechanical treatment. Certainly the concept of an activation energy is valid. We have found that for energies less than a "threshold", the reaction cross section is negligibly small. Such an energy dependence for the cross section will evidently give rise to an activation energy. The "threshold" is the incident relative translational energy that the system must have in order to reach a "reactive region;" that is, for the atom and molecule to get sufficiently close so that reaction will occur with a significant probability. One way of defining the reactive region is as the region in which the transition matrix element has an appreciable amplitude. From the calculations, this appears to be a region with a radius of about 2 a.u.

Another assumption that is used in ordinary rate theory is that for systems in which the potential energy is a minimum for the three atoms along a line, the reactions proceed through a linear configuration. While it is impossible that a reaction occurs only in an exactly linear configuration, near linear configurations do seem to be dominant in the $(H,H_2)$ system, particularly at energies near threshold. Evidence presented in the quantum-mechanical calculation shows that most of the reaction comes from a cone with less than 40° deviation from linearity, and the adiabatic molecular wave function shows that the molecule tends to line up itself

with the incoming atom. Furthermore, the quantum-mechanical linear model results are in very good agreement with the complete distorted wave calculation.

A point that plays an important role in the direct interaction theory is the effective two-body potential (optical potential) for the collision between atom and the molecule. For a given energy, the nature of the potential determines how close the particles can come together. As we have seen,[16] the two-body potential is difficult to evaluate uniquely, and different alternatives are possible according to how much translational energy is transferred to and from the energy of vibration and rotation. The exact answer can come only from the complete solution of the three-body problem. However, the calculations that we have done represent the two extremes of a real approximation to the optical potential. In one case, we have assumed that the initial molecule is unaffected by the incoming atom and in the other, that the initial molecule adiabatically follows the incoming atom. It is the latter calculation that appears more reasonable in terms of the characteristic times involved. However, the adiabaticity and resulting energy transfer depends on incident velocity and, therefore, on the total energy of the system. This suggests that the concept of an energy-dependent potential may be useful for the molecular collisions. We have found that not only the spherical part of the potential can change, but the higher harmonics may do so as well. Since the latter are responsible for molecular excitation, it appears that such an energy dependent potential should play a part in the study of inelastic molecular collisions, as well.

### (d) Antisymmetrization Process

In all of the preceding discussion, we have assumed that three particles are distinguishable and that only the reaction A+BC→AB+C has to be considered. Since the reaction A+BC→AC+B yields exactly equivalent results for the $H+H_2$ system, the reported total cross section values include this factor of two. However, the Pauli exclusion principle has not been explicitly introduced into the calculation. This is permissible because the necessary antisymmetrization can be applied to the T-matrix elements obtained from the unsymmetrized calculation. It is well known that such a process will mix the amplitudes of the direct and the exchange scattering. Thus, even the experimental measurements of the elastic scattering include contributions from the reactive process, though this term is relatively small for the present case. Also, a consideration of the nuclear spin statistics is required to relate the quantum-mechanical cross sections to the measured para→ortho conversion rate constants.[38]

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# APPENDIX

## Brief Description of the Computation

Because five-dimensional integrals must be evaluated in the present formulation of the distorted wave Born approximation and the number of machine operations required goes as the fifth power of the number of points used in each dimension, much effort was expended in preparing an efficient program. As an illustration, we give a brief description of the program used to calculate the reactive scattering amplitude $A_\ell$.

The total wave function which is approximated by the elastically scattered waves is summed up according to Eq. (30). The radial part $L_\ell(r)$ is normalized to

$$L_\ell(r) = (\cos\delta_\ell j_\ell(kr) - \sin\delta_\ell N_\ell(kr)) \tag{A1}$$

in the region where $V(r)=0$, with the phase shifts $\delta_\ell$ calculated by the method reported previously.[16] Legendre polynomials, spherical Bessel ($J_\ell$) and Neumann ($N_\ell$) functions are computed with their standard recursion formulas. The real and imaginary parts of the total wave function are stored separately in two three-dimensional tables with 3360 entries each. A table-look-up routine is used to interpolate when the required value is not at an entry point.

The numerical integration is done by the method of Gaussian quadrature.[40] The five-dimensional integration is programmed into a loop of five interlocked one-dimensional integration routines. The program is so written that the most time-consuming part, namely the potential evaluation, is carried out a minimum number of times.

The radial part of the molecular wave function is obtained with a one-dimensional Schrödinger equation solution routine provided by J. Cooley.[41] The angular part for the adiabatic molecule is calculated as described previously.[16] The resulting values are entered in two-dimensional arrays in preparation for the numerical integration.

Because the IBM 7094, which was used for the calculation, is too small for the entire program, the program is written as a chain job with three links. In the first link, the tables of total wave functions are prepared and the Gaussian points and weights are determined. In the second link, all quantities depending on $\ell$ [see Eq. (42)] are calculated. In the third link, the numerical integration is performed. After one $A_\ell$ is obtained, it is stored. Link 2 is then called in again and $\ell$ is increased by 1. The process is repeated until $A_\ell$ is negligibly small. Then all $A_\ell$'s are summed up according to Eq. (40), which yields the desired scattering amplitude.

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# Figure Captions

Fig. 1 Definition of Symbols

Fig. 2 Differential cross-sections of the reactive scattering of $H + H_2$ system. The solid line is obtained by DWB approximation for $J = o$ to $J' = o$ transition. The dotted line is from the classical trajectory calculation for $J = o$ to all $J'$ states.

Fig. 3 Contribution of each orbital angular momentum $\ell$ to the reactive cross-section at incident energy of 0.5 ev.

Fig. 4 Fractional contribution of different configurations of $H_3$ system to the total reactive cross-section.

Fig. 5 Differential cross-section of the reactive scattering of $H + H_2$ system according to the linear model.

Fig. 6 Differential cross-section of the reactive scattering of $H + H_2$ at different incident energies according to the linear model.

Fig. 7 Energy dependence of the total reactive cross-sections of $H + H_2$ between incident energy 0.3 and 0.6 ev. according to the linear model. The triangles are from the complete DWBA calculation.

Fig. 8 Energy dependence of the total reative cross sections of $H + H_2$ between incident energy of 0.3 and 1.1 eV according to the linear model.

Table I. Total Cross Section (J = o, J' = .) by DWB Approximation.

| Relative Energy | Unperturbed Model | Adiabatic Model |
|---|---|---|
| ev | a.u. | a.u. |
| 0.5 | 0.009 | 0.20 |
| 0.33 | - | 0.027 |
| 0.21 | - | 0.0001 |

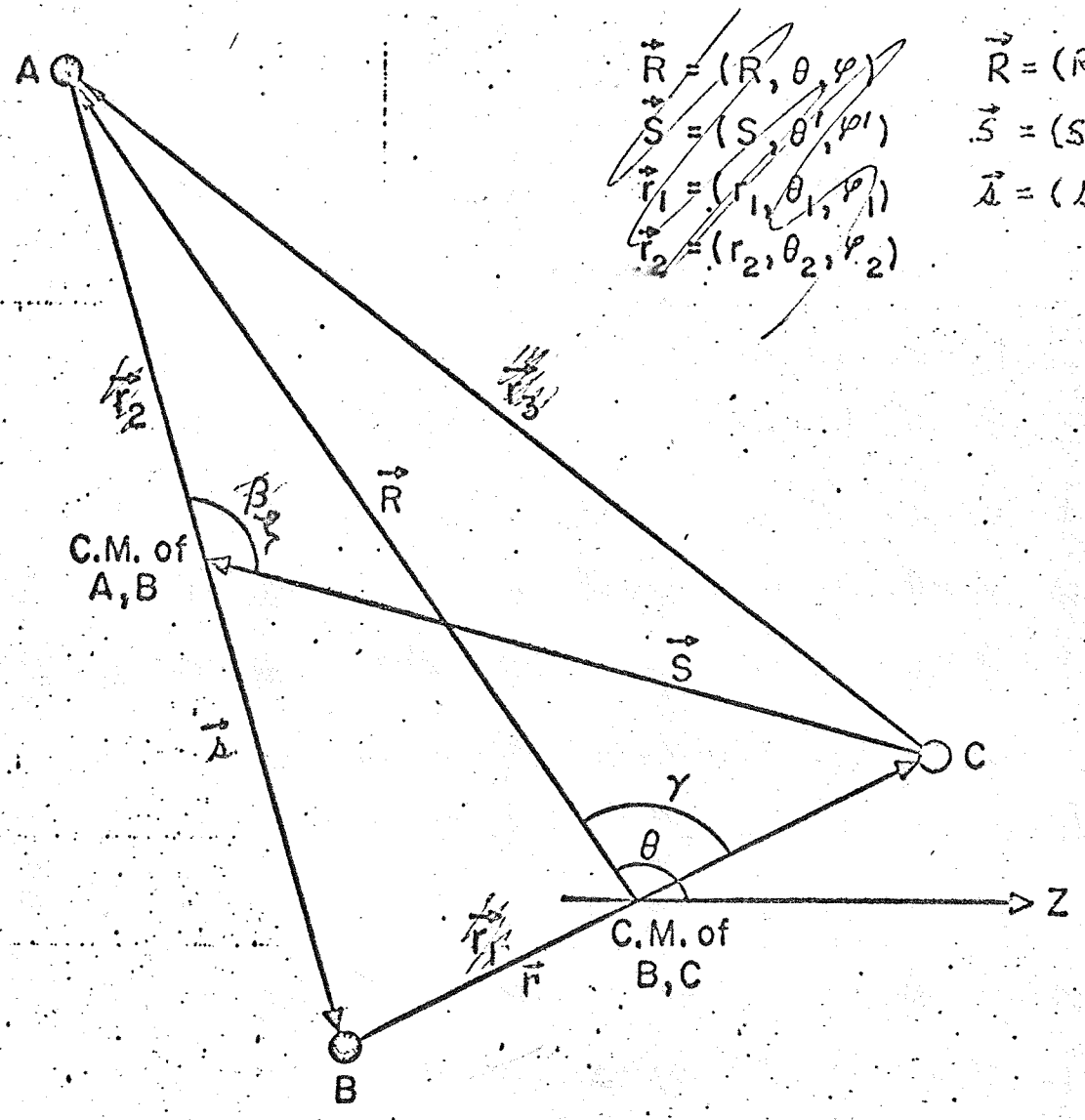

A
B
C
C.M. of A,B
C.M. of B,C
Z
$\vec{R} = (R, \theta, \varphi)$
$\vec{S} = (S, \theta', \varphi')$
$\vec{r}_1 = (r_1, \theta_1, \varphi_1)$
$\vec{r}_2 = (r_2, \theta_2, \varphi_2)$
$\vec{R} = (R, \theta, \phi)$
$\vec{S} = (S, \bar{\theta}, \bar{\phi})$
$\vec{\Delta} = (\Delta, \theta_1, \phi_1)$
$\vec{r}_2$
$\vec{r}_3$
$\vec{R}$
$\beta$
$\vec{S}$
$\vec{\Delta}$
$\gamma$
$\theta$
$\vec{r}_1$
$\vec{r}$

Fig. 1

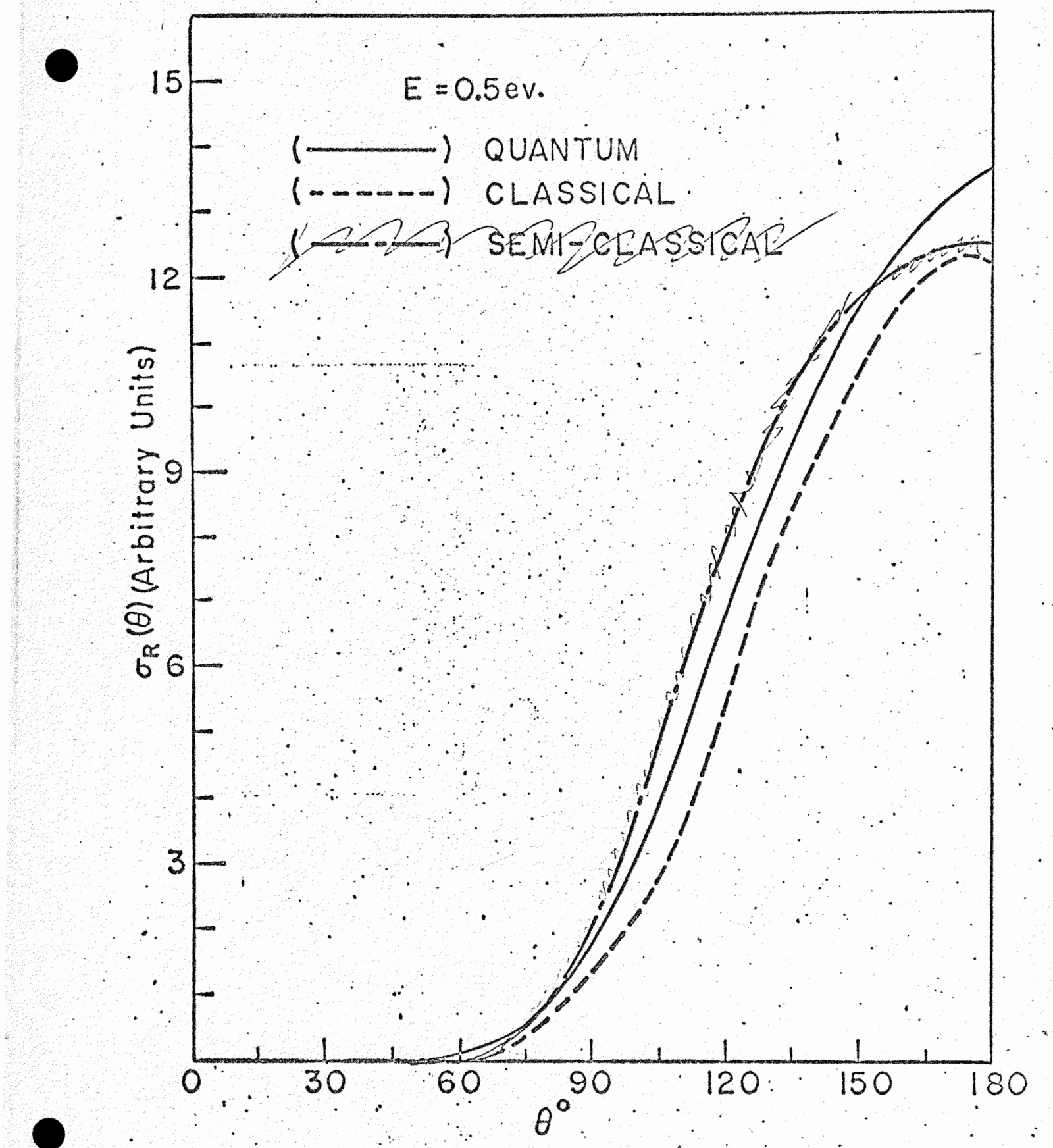

E = 0.5 ev.
(———) QUANTUM
(- - - - - -) CLASSICAL
(— - — - —) SEMI-CLASSICAL
$\sigma_R(\theta)$ (Arbitrary Units)
15
12
9
6
3
0
30
60
90
120
150
180
$\theta°$

Fig. 12

Fig 2

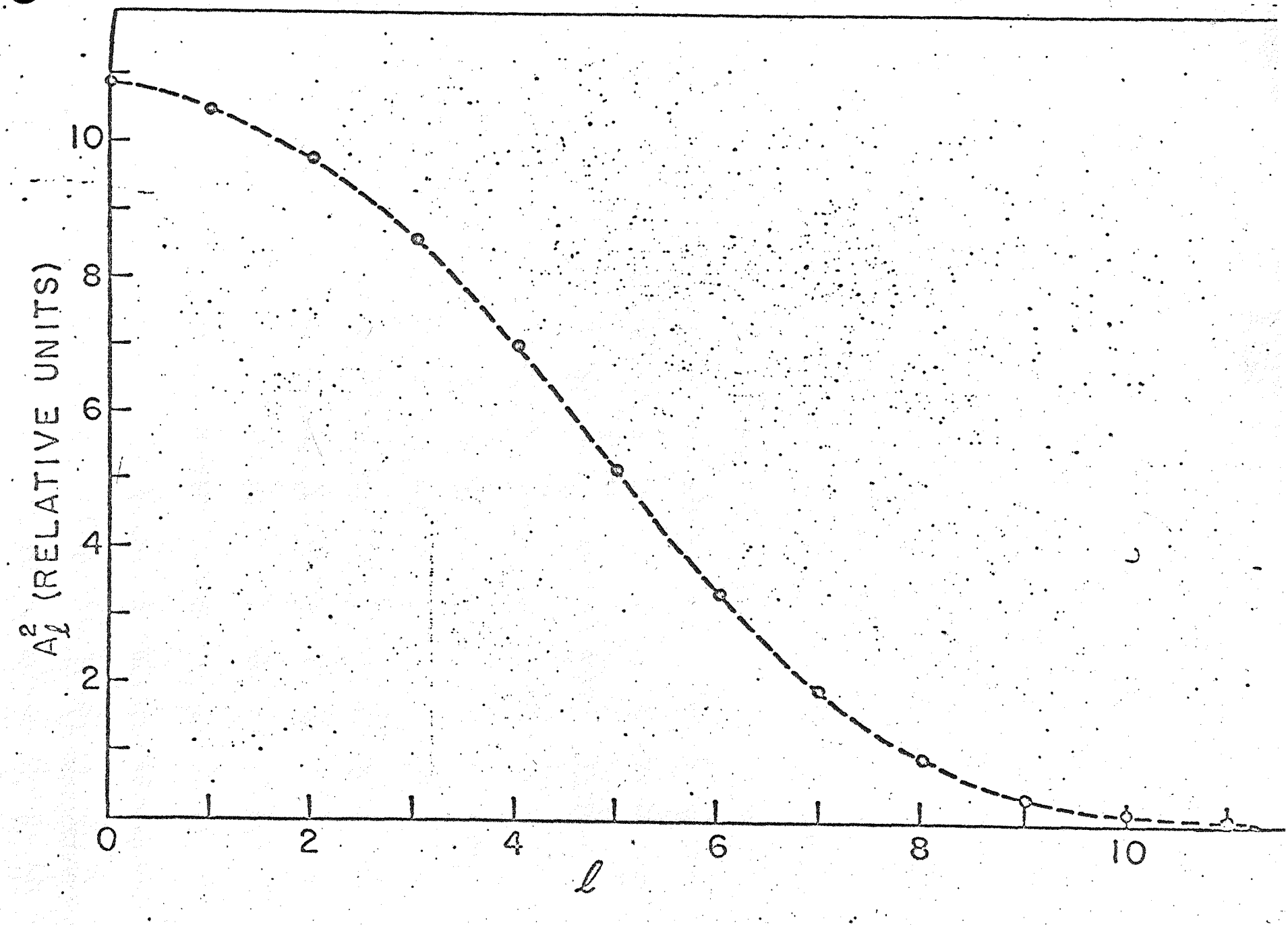
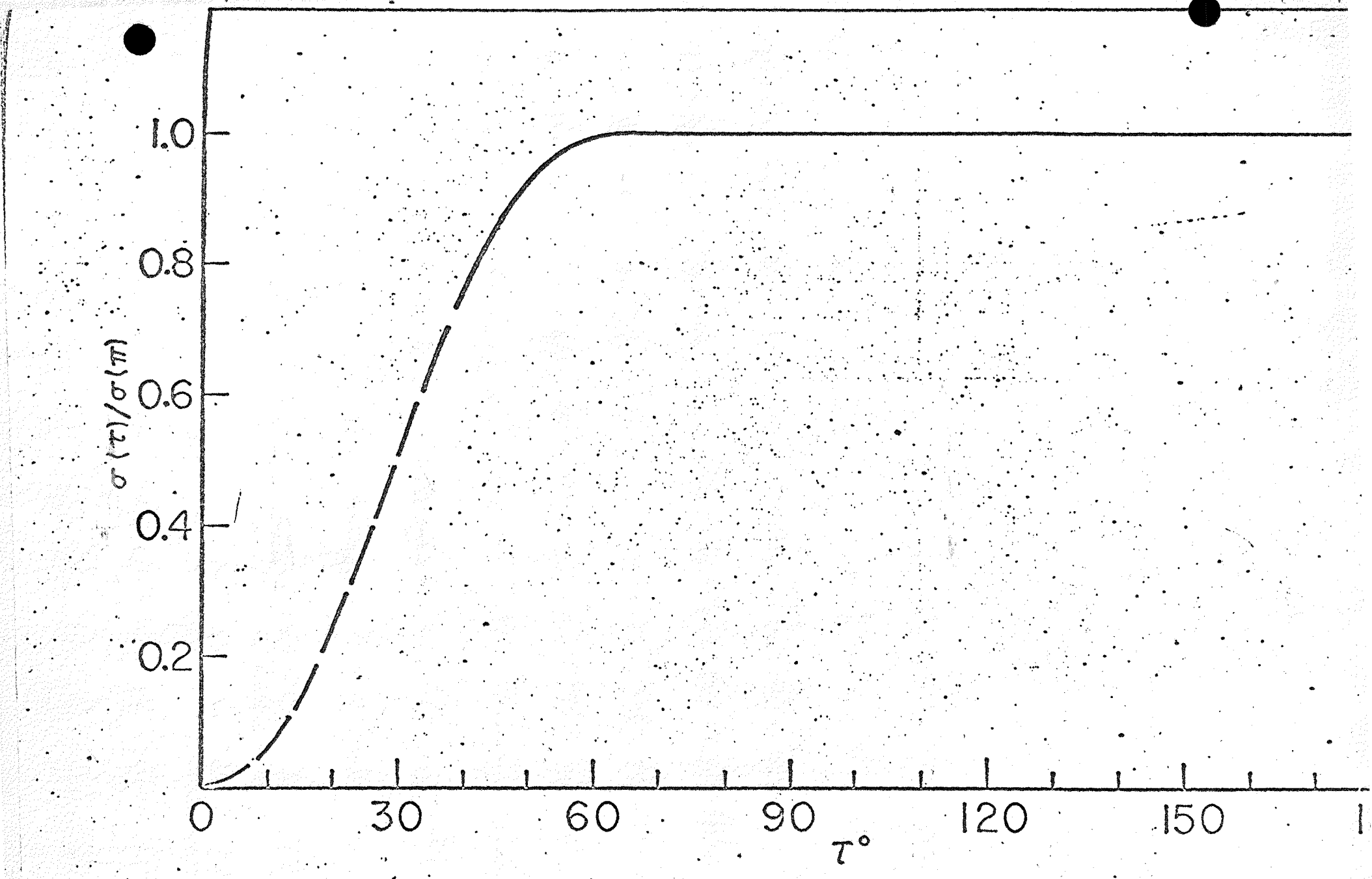



Fig. 3

(Fig. 3)




~~Fig. 14~~

Fig 4

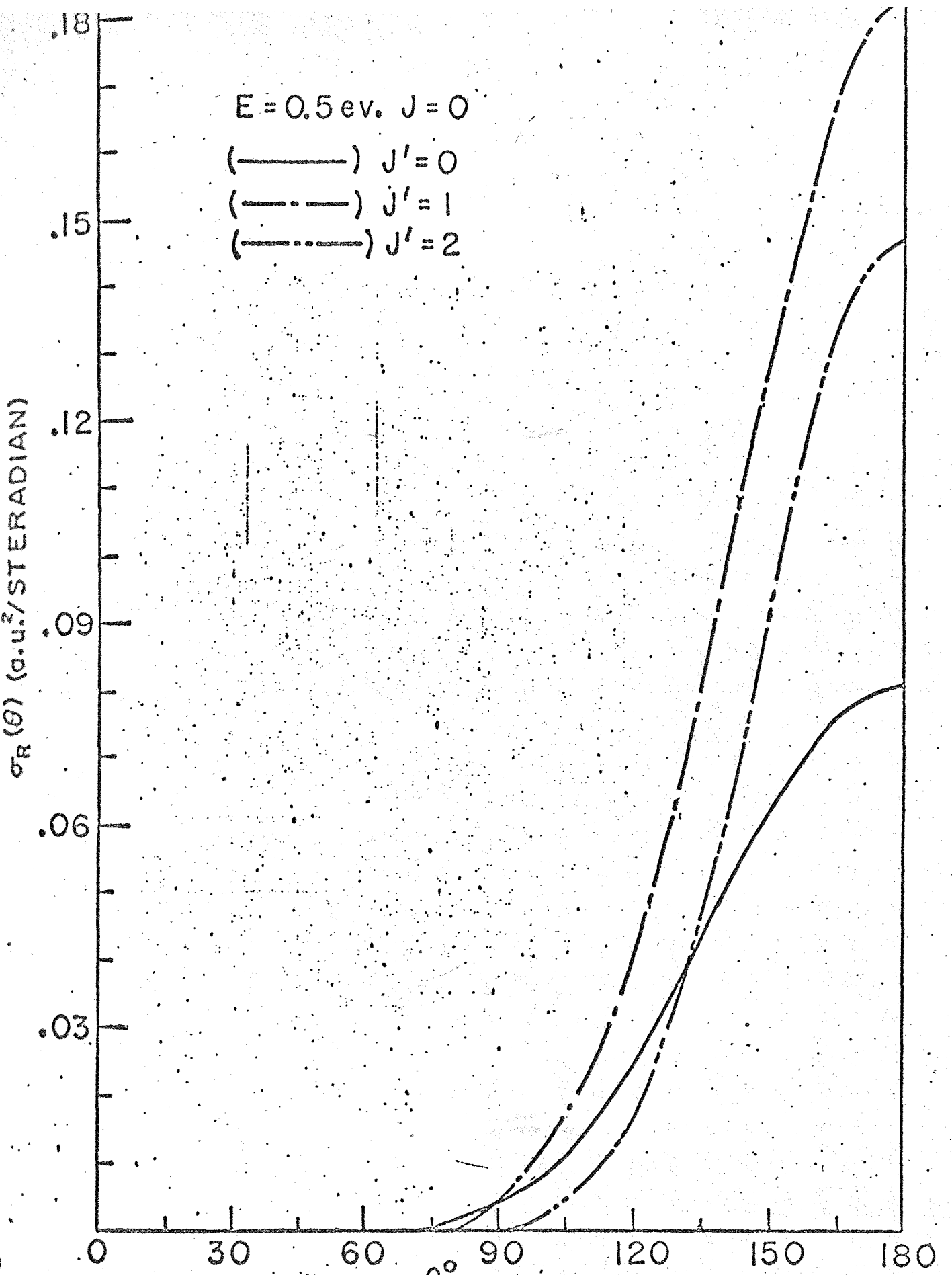

E = 0.5 ev. J = 0
(———) J' = 0
(—·—) J' = 1
(—··—) J' = 2
.18
.15
.12
.09
.06
.03
σR (θ) (a.u.²/STERADIAN)
0
30
60
90
120
150
180
θ°

Fig. 13 Figs

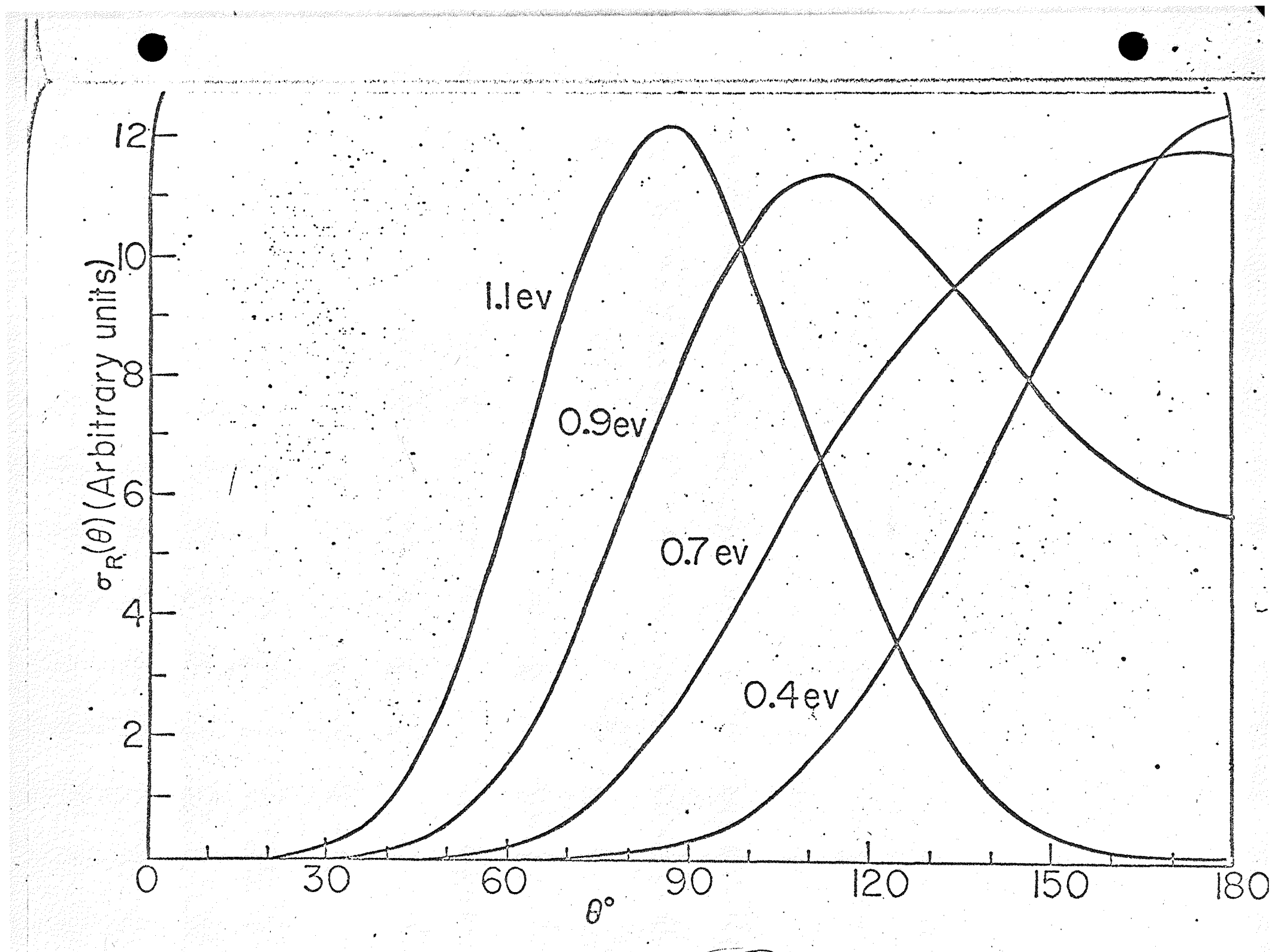

12
10
8
6
4
2
$\sigma_R(\theta)$ (Arbitrary units)
1.1ev
0.9ev
0.7 ev
0.4ev
0
30
60
90
120
150
180
$\theta°$

Fig. 16 (Fig 6)

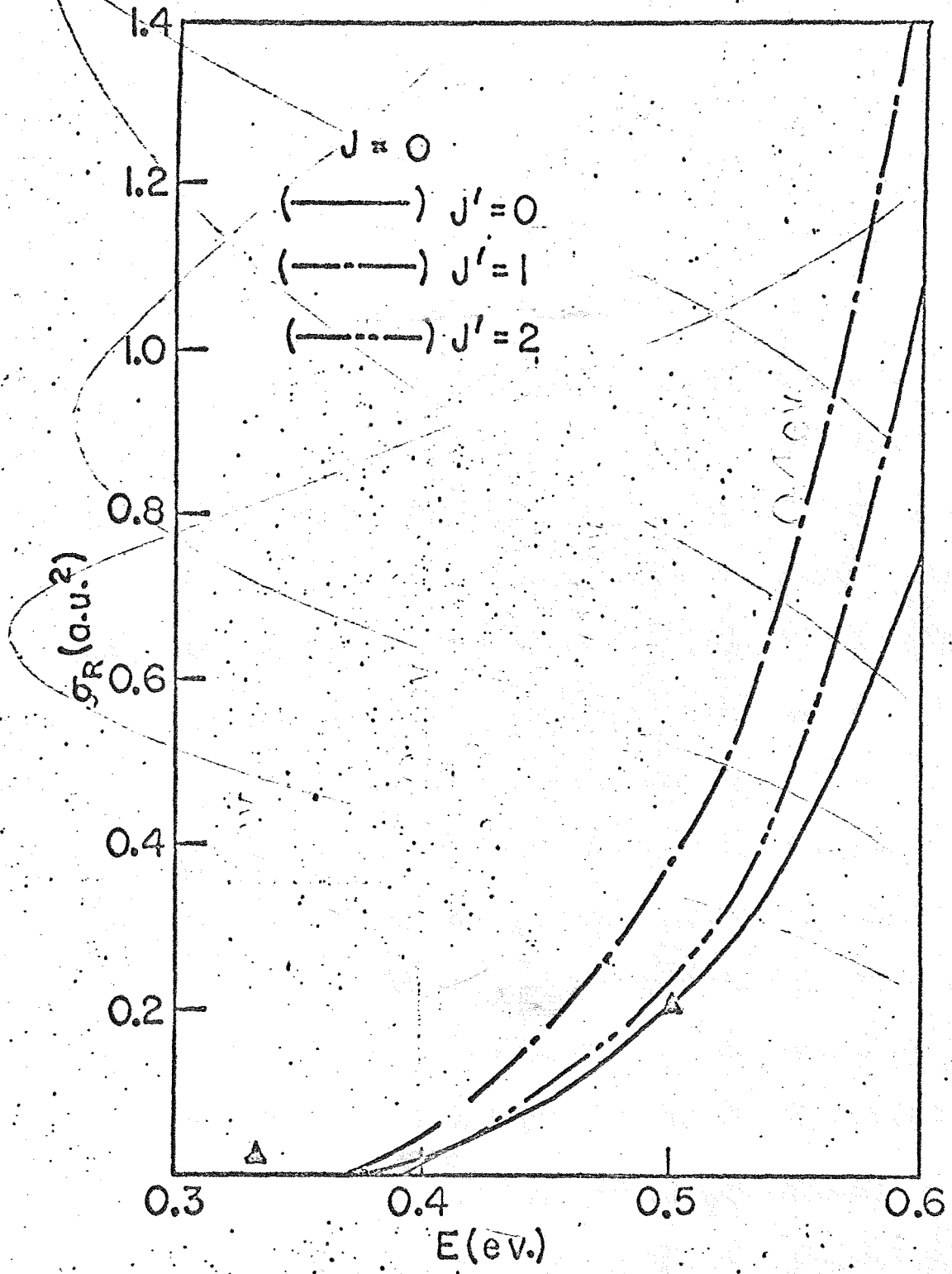



Fig. 17

Fig. 7

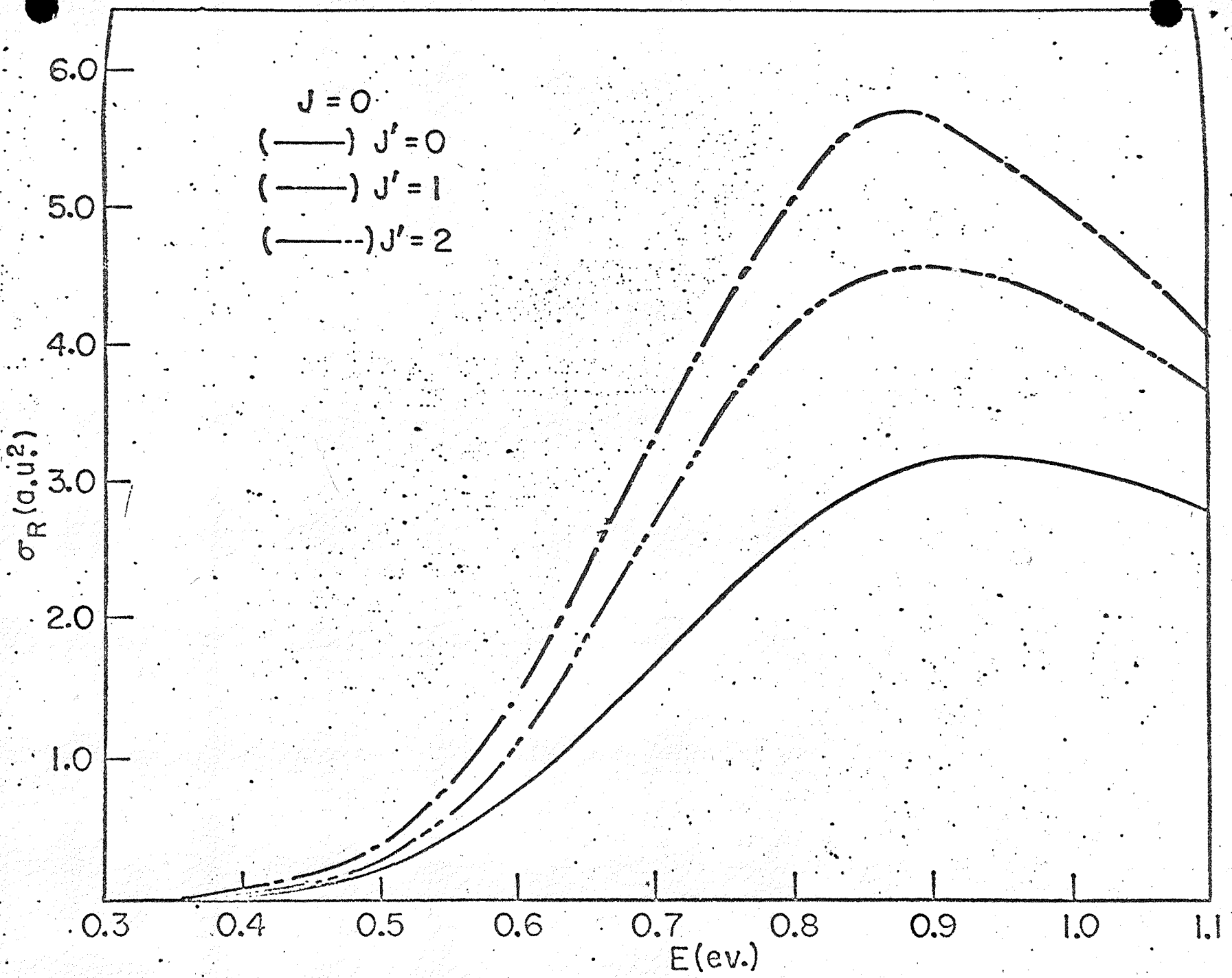



Fig. 18

(Fig. 8)