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TECHNICAL MEMORANDUM 560

JANUARY 1967

**CALCULATION OF SCATTERING AND REACTION
CROSS SECTIONS**

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ABSTRACT

The following papers are presented in this report:

1. Operator for Time Delay Induced by Scattering
2. A Note on Scattering Variational Principles
3. Integral Equations for Multi-Channel Collisions
4. Calculation of Dissociative Attachment in Hot O_2
5. Quasi-Adiabatic Molecular States: An Alternative to the Non-Crossing Rule
6. Theory of Resonant Dissociative Recombination
7. Formulation of the Two-State Problem in Terms of Adiabatic Potential Curves
8. Treatment of Angular Momentum in Momentum Space
9. On the Slope of Energy Curves as They Enter the Continuum

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I. INTRODUCTION

A. OBJECTIVE

The aim of the work reported here is to:

1. Review the available theoretical and experimental data on the reactions that control the electron density in missile wakes and in the environment surrounding nuclear bursts.
2. Supplement this by calculating the cross sections (reaction rates) for specific reactions of importance in these problem areas. (In its initial stages, the program has studied reactions in atmospheric gases such as dissociative recombination [Example: $\text{NO}^+ + e \rightarrow \text{N} + \text{O}$] and related processes.)
3. Compute other reactions as requested by ARPA.
4. Develop general computational techniques designed to improve the accuracy and reliability of calculations of this type.

B. RELEVANCE TO THE DEFENDER PROGRAM

The program at Defense Research Corporation is directed towards the analyses of reaction rates that are directly applicable to several critical problem areas in the Defender program. Some of these are:

1. Radar return from missile wakes.
2. Nuclear fireball clutter and scintillation effects.
3. The expansion of nuclear debris at high altitudes.
4. Atmospheric disturbances introduced by nuclear weapons.

The objective at Defense Research Corporation has been to devise practical computational techniques for estimating the cross sections of the critical reactions connected with these problems. The personnel

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assigned to this task, well qualified by training and experience to undertake this work, include:

Dr. B. A. Lippmann, Principal Investigator (half-time),
Dr. T. F. O'Malley (full time),
Dr. P. J. Redmond (half-time).

C. SYNOPSIS OF WORK ACCOMPLISHED

At the present time, the work is proceeding along two lines. The main emphasis is being placed on numerical analysis of specific reactions. However, auxiliary formal studies relating to questions arising in the course of attempting the numerical calculations are also being carried out.

While some aspects of the work have not yet been completed, or are still in the process of being written up, a fair sampling of the work accomplished during the 1966 period is contained in the list of reports and journal articles given in the Table of Contents. Copies of all these documents are attached. In addition, technical assistance in connection with the ARPA A&M Physics Program has been furnished as requested.

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II. COMPANY REPORTS AND JOURNAL ARTICLES

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OPERATOR FOR TIME DELAY INDUCED BY SCATTERING *

by

B. A. Lippmann

ABSTRACT

The operator that gives the time delay induced by a scattering process is exhibited explicitly.

It is well known that the time delay induced by a scattering process is given by the energy derivative of the phase shift.¹ Some time ago,² we observed that this theorem can be put in the "suggestive" form $S^{-1}rS$, where r is interpreted as an "operator," equivalent, in an energy representation, to differentiation with respect to the energy. It is the purpose of this paper to make this relationship precise by exhibiting the time-delay operator explicitly.

That such an operator might exist is suggested by the action and angle variables of classical theory. For, if the action variable J_1 is identified with the energy, the conjugate angle variable ϕ_1 has the

* Published in Phys. Rev. 151, 1023 (1966).

¹ This appears to have first been shown quantum-mechanically by E. P. Wigner, Phys. Rev. 98, 145 (1955), although relationships of this sort are well known in filter theory, where the frequency derivative of the phase characteristic gives the time required for a pulse of energy to pass through the filter [Radiation Laboratory Series (McGraw-Hill Book Company, Inc., New York, 1948), Vol. 8, p. 155]. A similar relation describes the spatial displacement of a wave packet upon reflection by a plane interface whose reflection coefficient is a function of the wave number parallel to the interface, L. M. Brekhovskikh, Waves in Layered Media (Academic Press Inc., New York, 1960), p. 105.

² See F. T. Smith, Phys. Rev. 118, 349 (1960), Eq. (45).

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equation of motion

$$\dot{\phi}_1 = \frac{\partial H}{\partial J_1} = 1, \quad (1)$$

which integrates to

$$\phi_1(t) = t + \phi_1(0). \quad (2)$$

One would expect that the first equation would have as its quantum-mechanical analog the conventional commutation relation that holds for conjugate variables, while the second equation, transcribed to quantum mechanics, would relate one of the quantum-mechanical operators to the time parameter. It is shown below that these expectations can be realized.

We first introduce the operator for the magnitude of the particle momentum

$$p = \left(p_x^2 + p_y^2 + p_z^2 \right)^{1/2} \quad (3)$$

and the operator representing the projection of the radial coordinate upon the momentum

$$r_p = (1/p)(p \cdot r). \quad (4)$$

These are analogous to the operators introduced by Dirac³ except that the roles of position and momentum have been exchanged.

As in Ref. 3, we easily find that these operators satisfy the commutation relation

$$[r_p, p] = i \quad (5)$$

and that the operator $r_p + i/p$, which is Hermitian, is canonically conjugate to p .

³ P. A. M. Dirac, The Principles of Quantum Mechanics (Oxford University Press, New York, 1958), p. 152.

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The time-delay operator τ is defined by

$$\tau = \frac{m}{2p} \left(r_p + \frac{1}{p} \right) + \left(r_p + \frac{1}{p} \right) \frac{m}{2p} . \quad (6)$$

For the free particle Hamiltonian, $H_0 = p^2/2m$, we find

$$[\tau, H_0] = i . \quad (7)$$

Although τ , as constructed in Eq. (6) above is formally Hermitian, some care must be taken in developing its properties, because of the fact that H_0 has a spectrum that is limited to positive values $(0, \infty)$.⁴ However, this circumstance does not impair the interpretation, which follows directly from Eq. (7), of τ as an energy derivative in a representation in which H_0 is diagonal: $r \rightarrow i\partial/\partial E$.

Calling the operator defined in Eq. (6) $\tau(0)$, we can also introduce the time-dependent operator

$$\begin{aligned} \tau(t) &= e^{iH_0 t} \tau(0) e^{-iH_0 t} \\ &= t + \tau(0) . \end{aligned} \quad (8)$$

The relations given in Eqs. (7) and (8) above are the quantum mechanical analogs of the classical Eqs. (1) and (2).

The application to the calculation of time delays is made by considering the matrix element

$$\left(\psi_a(t), \tau(0) \psi_a(t) \right) , \quad (9)$$

where the state vector $\psi_a(t)$ is the scattered wave packet, evaluated for times after the scattering process has been completed. The time dependence of this state vector is then given by the free-particle Hamiltonian alone: $\psi_a(t) = e^{-iH_0 t} \psi_a(0)$: here, the last factor represents the

⁴ For example, the operator i has no eigenfunctions; see W. Pauli, Handbuch der Physik (Springer-Verlag, Berlin, 1958), Vol. 5/1, p. 63.

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scattered-state vector extrapolated back to zero time.

In the following, both the incident and scattered wave packets are assumed to be normalized to unity. Since the scattered state is connected with the initial state vector $\phi_a(0)$ by the S matrix, (9) can be evaluated as below:

$$\begin{aligned} & \left(\psi_a(0), e^{iH_0 t} \tau(0) e^{-iH_0 t} \psi_a(0) \right) \\ &= \left(\psi_a(0), \left[t + \tau(0) \right] \psi_a(0) \right) \\ &= t + \left(\phi_a(0), S^{-1} \tau(0) S \phi_a(0) \right). \end{aligned} \quad (10)$$

If the S matrix has the form $S = e^{2i\delta(E)}$, in an energy representation the time delay operator becomes equivalent to energy differentiation, and we find, as a final result

$$\left(\psi_a(t), \tau(0) \psi_a(t) \right) = t - 2 \frac{\partial \delta(E)}{\partial E} + \left(\phi_a(0), \tau(0) \phi_a(0) \right). \quad (11)$$

In this form the interpretation of the energy derivative of the phase shift as the time delay induced by the scattering process is apparent.

I am indebted to Professor Massey of University College, London, for his generous hospitality extended over part of the period during which these ideas were clarified.

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A NOTE ON SCATTERING VARIATIONAL PRINCIPLES*

by

B. A. Lippmann

ABSTRACT

The Schwinger variational principle is converted into a slightly modified form of the Kohn-Hulthen variational principle. A generalization of the new form, valid for rearrangement collisions, is given.

DIRECT COLLISIONS

We start with the Schwinger variational principle

$$T_{ba} = (\phi_b, V \psi_a^{(+)} + (\psi_b^{(-)}, V \phi_a) - (\psi_b^{(-)}, |V - VG_0 V| \psi_a^{(+)}) , \quad (1)$$

where

$$G_0 = \frac{1}{\lambda_a - H_0} ; \quad \lambda_a = E_a + i\epsilon ; \quad \epsilon > 0 . \quad (2)$$

The last two terms on the right side of (1) may be combined to yield:

$$\left(\psi_b^{(-)}, V \left| \phi_a - \psi_a^{(+)} + G_0 V \psi_a^{(+)} \right| \right) = - \left(\psi_b^{(-)}, (\lambda_a - H) \left| \phi_a + G_0 V \psi_a^{(+)} \right| \right) + i\epsilon (\psi_b^{(-)}, \phi_a) . \quad (3)$$

The last term above may be dropped since it vanishes in the limit $\epsilon \rightarrow 0$.

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Treating the first term on the right side of (1) similarly,

$$\left(\phi_b, V \psi_a^{(+)} \right) = \left(\phi_b, (\lambda_a - H_0) \left| \phi_a + G_0 V \psi_a^{(+)} \right| \right) - i\epsilon (\phi_b, \phi_a) \quad (4)$$

where, as before, the last term vanishes in the limit $\epsilon \rightarrow 0$.

As a consequence, (1) takes on the new form

$$T_{ba} = \left(\phi_b, (\lambda_a - H_0) \left| \phi_a + G_0 V \psi_a^{(+)} \right| \right) - \left(\psi_b^{(-)}, (\lambda_a - H) \left| \phi_a + G_0 V \psi_a^{(+)} \right| \right) \quad (5)$$

where the limit $\epsilon \rightarrow 0$ is understood.

It is clear that $\psi_a^{(+)}$ and the quantity in the {---} are equally suitable as trial functions and are equal for the exact state vector. Hence, if we regard {---} as the trial function, and symbolize it by $\psi_a^{(+)}$, when we pass to the limit $\epsilon \rightarrow 0$, a slightly modified form of the Kohn-Hulthen variational principle results:

$$T_{ba} = \left(\phi_b (E - H_0) \psi_a^{(+)} \right) - \left(\psi_b^{(-)}, (E - H) \psi_a^{(+)} \right) , \quad (6)$$

where E is the common energy of states a and b .

Starting from (1) again, and combining the terms involving $\psi_b^{(-)}$, we obtain

$$T_{ba} = \left((E - H_0) \psi_b^{(-)}, \phi_a \right) - \left((E - H) \psi_b^{(-)}, \psi_a^{(+)} \right) . \quad (7)$$

The variational principle (6) differs slightly from the usual Kohn-Hulthen form; the first term on the right is more conventionally expressed as $(T_{ba})_{\text{trial}}$. The present form automatically insures that this term emerges. A similar remark holds for (7).

It will be noted from (1) that the presence of V limits all integrals to the region where the potential differs from zero. The integrals in (6)

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and (7) should therefore be restricted to the same regions. If the trial functions are constructed to represent free particle motion outside the region where the potential is different from zero, this restriction of the region of integration is automatically accomplished in (6) and (7).

Although the manner of derivation of (6) and (7) from (1) insures that the stationary properties of (1) are maintained in the forms (6) and (7), it is a simple matter to verify directly that (6) and (7) are stationary expressions for T_{ba} when the state vectors are varied about their exact values.

REARRANGEMENT COLLISIONS

The foregoing may be extended to rearrangement collisions by introducing a channel index ($\alpha = 1, 2, \dots, N$) on the decomposition of the Hamiltonian

$$H = H_{0,\alpha} + V_{\alpha} \quad (8)$$

as well as the state vectors. When this is done, the variational principle for the amplitude scattered from channel α , state a , to channel β , state b , can be put in the two alternative forms:

$$\begin{aligned} T_{b,\beta;a,\alpha} &= \left(\phi_{b,\beta}, (E-H_{0,\beta}) \psi_{a,\alpha}^{(+)} \right) - \left(\psi_{b,\beta}^{(-)}, (E-H) \psi_{a,\alpha}^{(+)} \right) \\ &= \left((E-H_{0,\alpha}) \psi_{b,\beta}^{(-)}, \phi_{a,\alpha} \right) - \left((E-H) \psi_{b,\beta}^{(-)}, \psi_{a,\alpha}^{(+)} \right). \quad (9) \end{aligned}$$

COMMENTS

The two forms given in (6) and (7) treat the initial and final states unsymmetrically. Clearly, a symmetrical form of the variational principle may be obtained by averaging (6) and (7), and similarly for the two forms given in (9).

The trial functions appearing in these variational principles correspond to diagonalizing the momenta of the incident and final states. If

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the potential is spherically symmetric, forms of the variational principles given above are easily obtained, in which the angular momentum is diagonal, by introducing the conventional resolution of plane waves to angular momentum eigenstates. In the new forms, the T-matrix for angular momentum, ℓ , is given by $-\frac{1}{\pi} e^{i\delta_\ell} \sin \delta_\ell$; only the radial parts of the Hamiltonian operators H_0 and H appear, and the wave functions are purely radial. To verify that the expressions for each angular momentum state, ℓ , are individually stationary, we assume that the state vector is given exactly in the plane wave form for all $\ell' \neq \ell$; varying the quantities referring to ℓ only, the stationary property of the original (plane wave) expression then insures that the terms involving ℓ alone constitute a stationary expression.

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INTEGRAL EQUATIONS FOR MULTI-CHANNEL COLLISIONS*

by

B. A. Lippman

ABSTRACT

Two new integral equations to describe multi-channel collisions are given: one uses an explicit cut-off radius; the other does not. The new integral equations possess symmetrical kernels, thereby facilitating the application of the Pauli principle and permitting the asymptotic scattered amplitude in each channel to be derived simply. The limit $\epsilon \rightarrow 0$ does not result in a "homogeneous" integral equation.

The integral equations appropriate to each of the channels in a multi-channel collision are here unified by the use of channel projection operators.¹ Two new integral equations result corresponding to the choice of two different types of channel projection operators used: one type uses an explicit cut-off radius and the other does not.

The new integral equations treat all channels on an equal basis; permit simple derivations of the asymptotic form of the scattered amplitude in each channel -- from which the transition matrix elements are easily identified; possess symmetrical kernels, thereby facilitating the application of the Pauli principle; and eliminate the difficulties in principle arising from the presence of "homogeneous" equations in some of the channels.²

* Submitted to ARPA for publication clearance.

¹ Related operators have previously been introduced by H. Feshbach, Ann. Phys. (N.Y.) 5, 357 (1958); 19, 287 (1962); and B. A. Lippmann, Lockheed Technical Report NONR 3368(00), 1964 (unpublished).

² This apparent lack of uniqueness in multi-channel collision theory has led to the introduction of the Fadeyev equations. There is no lack of uniqueness if $\epsilon \neq 0$.

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The derivation is given in a general form and also illustrated for the case of electron scattering by atomic hydrogen. The electrons are first considered distinguishable: the Pauli principle is taken into account later.

For electron-H scattering, there are four channels. Assuming shielded Coulomb potentials, channel 1 corresponds to electron 1 moving freely and electron 2 interacting with the proton; channel 2 corresponds to electron 2 moving freely and electron 1 interacting with the proton; channel 3 corresponds to both electrons moving freely; channel 4 corresponds to both electrons interacting with the proton and, if convenient, also with each other.³ There is some arbitrariness in the division of the interactions between $H_{o,\alpha}$ and V_α , where $H = H_{o,\alpha} + V_\alpha$ ($\alpha = 1,2,3,4$).

The basis vectors in each channel are

$$\begin{aligned}\phi_{a,1}(1,2) &= \xi_a(2) \chi_a(1) \\ \phi_{a,2}(1,2) &= \eta_a(1) \chi_a(2) \\ \phi_{a,3}(1,2) &= \chi_a(1) \chi_a(2) \\ \phi_{a,4}(1,2) &= \zeta_a(1) \mu_a(2)\end{aligned}\tag{1}$$

where the χ 's correspond to particle wave functions and the remaining symbols describe interacting wave functions. Each ϕ above is an eigenfunction of the corresponding $H_{o,\alpha}$.

Assuming the incident wave is in channel 1, the integral equation for the total wave function is

$$\psi_{a,1}^{(+)} = \phi_{a,1} + G_{o,1} V_1 \psi_{a,1}^{(+)}\tag{2}$$

³ In particular, channel 4 can be defined to include a zero width resonant state, with V_4 being responsible for the energy shift and lifetime.

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where

$$G_{0,1} = \frac{1}{\lambda_a - H_{0,1}} ; \quad \lambda_a = E_a + i\epsilon ; \quad \epsilon > 0 . \quad (3)$$

In channels 2,3, and 4, we have (in the limit $\epsilon \rightarrow 0$)⁴

$$\begin{aligned} \psi_{a,1}^{(+)} &= G_{0,2} V_2 \psi_{a,1}^{(+)} \\ &= G_{0,3} V_3 \psi_{a,1}^{(+)} \\ &= G_{0,4} V_4 \psi_{a,1}^{(+)} . \end{aligned} \quad (4)$$

The integrations in coordinate space consist of the direct products of the individual coordinate spaces of electrons 1 and 2, which we divide into channels as follows. In each space, we introduce a distance R around the target. Let $R_I(1)$ be the operator that projects onto the space of particle 1 interior to R ; similarly, let $R_E(1)$ project onto the space of particle 1 exterior to R . These are the "internal" and "external" regions of 1. For any value of the total energy, R can be chosen large enough so that if one examines the wave functions of the bound states energetically possible in each channel, these wave functions are essentially contained within R .

We define four channel projection operators corresponding to the four channels that are possible in this special case:

$$\begin{aligned} C_1 &= R_I(2) R_E(1) ; & C_2 &= R_I(1) R_E(2) \\ C_3 &= R_E(1) R_E(2) ; & C_4 &= R_I(1) R_I(2) . \end{aligned} \quad (5)$$

The channel operators are mutually exclusive and their sum covers the direct product space completely;

$$C_i C_j = C_i \delta_{ij} ; \quad \sum_i C_i = 1 . \quad (6)$$

⁴ B. A. Lippmann, Phys. Rev. 102, 264 (1956).

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We now multiply Eq. (2) by C_1 , and the successive lines of (4) by C_2 , C_3 , and C_4 , and add, thereby obtaining the first of the integral equations we have been seeking

$$\psi_{a,1}^{(+)} = C_1 \phi_{a,1} + \sum_{\alpha} C_{\alpha} G_{o,\alpha} V_{\alpha} \psi_{a,1}^{(+)} \quad (7)$$

In the limit $\epsilon \rightarrow 0$, the second term on the right yields the scattered amplitude in each channel. That is, the projection operators effect a separation between those states which only exist in the region internal to R and those which exist in the external region as well: these are the discrete and continuum states respectively. If R has been chosen large enough, the discrete states in the internal region that are energetically accessible maintain their full orthogonality properties unimpaired. The continuum states in the external region that combine with these bound states to conserve energy are unaffected by starting the integration at a finite value of R ; the continuum states that do not conserve energy are exponentially damped in the external region. Thus, as R approaches infinity, these exponentially damped states contribute nothing. For the "propagating" states in the external region, R may be permitted to approach zero.

Introducing the basis vectors for each channel explicitly, (7) becomes

$$\psi_{a,1}^{(+)} = C_1 \phi_{a,1} + \sum_{\alpha} \sum_b \frac{C_{\alpha} \phi_b}{\lambda_a - E_b} T_{b,\alpha;a,1} \quad (8)$$

where the transition amplitudes are given by

$$T_{b,\beta;a,\alpha} = (\phi_{b,\beta} V_{\beta} \psi_{a,\alpha}^{+}) \quad (9)$$

We have assumed distinguishable particles in deriving (8). However, if the particles are indistinguishable, (7) may be adapted to reflect this explicitly by multiplying both sides by the proper symmetrization or anti-symmetrization operator, s . With the limit $\epsilon \rightarrow 0$ understood, (8) is then

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replaced by

$$\psi_{a,1}^{(+)} = s C_1 \phi_{a,1} + \sum_{\alpha} \sum_b \frac{C_{\alpha} \phi_{b,\alpha}}{\lambda_a - E_b} (\phi_{b,\alpha}, V_{\alpha} s \psi_{\epsilon,1}^{(+)}). \quad (10)$$

The sum in (10) includes states that differ only by an interchange of particles 1 and 2. If the summation is restricted so that these states are excluded -- that is, the summation is only over "distinct" channels -- (10) becomes

$$\psi_{a,1}^{(+)} = s C_1 \phi_{a,1} + \sum_{\substack{\alpha, b \\ \text{"distinct"} \\ \text{states}}} \frac{s C_{\alpha} \phi_{b,\alpha}}{\lambda_a - E_b} (\phi_{b,\alpha}, V_{\alpha} s \psi_{a,1}^{(+)}). \quad (11)$$

Thus the transition amplitude, when the Pauli principle is operative, is given by

$$T_{j,\beta;a,\alpha} = (\phi_{b,\beta}, V_{\beta} s \psi_{a,\alpha}^{(+)}). \quad (12)$$

The projection operators defined so far correspond to a definite choice of a cut-off radius. However, (8) also holds for the channel projection operators, defined below, which are independent of the cut-off radius.

These C_{α} are defined in the terms of the particle energies as follows. In each channel, say " α ," the corresponding $H_{o,\alpha}$ defines the energies of particles 1 and 2 -- when one of them is in the asymptotic region -- unambiguously. We can therefore redefine the C_{α} :

$$\begin{aligned} C_1 &= \eta(-E_2) \eta(E_1) & ; & & C_2 &= \eta(-E_1) \eta(E_2) \\ C_3 &= \eta(E_1) \eta(E_2) & ; & & C_4 &= \eta(-E_1) \eta(-E_2) \end{aligned}$$

$$2r(x) = 1 + \frac{x}{|x|}. \quad (13)$$

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The previous considerations hold unchanged for the new definitions of the channel projection operators, in particular, (8) no longer requires the introduction of a cut-off radius.

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CALCULATION OF DISSOCIATIVE ATTACHMENT IN HOT O_2^*

by
T. F. O'Malley

ABSTRACT

The very striking temperature dependence of the dissociative attachment cross sections found experimentally in O_2 has been reproduced by a semi-empirical calculation, assuming a Maxwell distribution of vibrational (v) and rotational (r) states. A recently derived expression for the cross section $\sigma_{v,r}$ is used, and the final state potential curve of O_2^-* is parametrized to fit the experiments. The temperature shift is found to be caused by the effect on excited vibrational states of the rapidly varying "survival probability," a measure of the competition between autoionization and dissociation. By-products of the calculation are the potential curve for the final dissociating state of O_2^-* together with an estimate of its autoionization width, $\Gamma_a(R)$, and also the contribution of this state to the total cross section for electron energy loss to vibrational excitation and dissociation.

It has been found experimentally by Fite et al.¹ that the cross section for dissociative attachment (DA) of electrons to O_2 has an extraordinarily large dependence on the temperature of the O_2 . The shift and broadening with temperature was such that at 300°K the cross section peak was shifted to lower energy by 1 eV while the apparent onset was reduced

* To appear in Phys. Rev., March 1967.

¹ W. L. Fite and R. T. Brackmann, Proc. 4th International Conference on the Ionization Phenomena in Gases, Paris, 1963, Vol I, p. 21.
W. L. Fite, R. T. Brackmann, and W. R. Henderson, IVth International Conference on the Physics of Electronic and Atomic Collisions, Science Bookcrafters, Inc., Hastings, N.Y. (1965), p. 100.

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by over 2 eV. The present calculation was done in an attempt to provide some understanding of this remarkable effect.

It is first assumed that the direct effect of the temperature (T) of the O₂ is to produce a Maxwell distribution of vibrational (v) and rotational (r) states. The cross section σ(T,E), where E is the electron energy, is then the Boltzmann average of the cross sections σ_{v,r}(E) from each of the individual excited states, thus

$$\sigma(T,E) = \sum_{v=v_{\min}}^{\infty} \sum_{r=r_{\min}}^{\infty} N e^{-(E_v+E_r)/kT} \sigma_{v,r}(E) \quad (1)$$

where N is the Boltzmann normalization factor, and E_v and E_r are the vibrational energy and rotational energies of the O₂ molecules, respectively. The quantities v_{min} and r_{min} are subject to the threshold requirement for the process, viz. E + E_v + E_r ≥ 3.6 eV, and the cross section σ_{v,r} is given by the theoretical expression²

$$\sigma_{v,r}(E) = \frac{4\pi^2 g}{k^2} \frac{\Gamma_{a,\chi}}{\Gamma_d} \left| \chi_v \left(R_E - i \frac{\Gamma_a}{\Gamma_d} \right) \right|^2 e^{-\rho} \quad (2)$$

The Γ_a, Γ_d and ρ as well as χ_v are evaluated at the final state turning point R_E(E,v,r). The exact definition of the quantities is given in Ref. 2. In particular, k is the electron's momentum, g is an angular momentum and spin factor. Γ_a and Γ_{a,χ} are the total and partial (for the ground state X) autoionization widths, i.e., Γ_a = Σ_j Γ_{a,j}. Γ_d is a width for dissociation, χ_v is the vibrational wave function, R_E the turning point is in vibrational units and ρ is twice the imaginary part of the final state phase shift ε_r. The factor e^{-ρ} is called the survival probability³ or survival factor. It is given approximately by

$$e^{-\rho} = \exp \left[- \int_{R_E}^{R_c} \Gamma_a(R) dR / \hbar v(R) \right] = \exp \left[- \int \Gamma_a(R) dt(R) / \hbar \right] \quad (3)$$

² T. F. O'Malley, Phys. Rev. 150, 14 (1966).

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where R_c is the point where Γ_a goes to zero, v is the velocity of dissociation and t the corresponding classical time. This factor results from the competition between autoionization and dissociation. Where the above expression is not sufficiently accurate, an exact expression can be used.³ The effect of rotation in (2) is implicit. It adds a centrifugal term to the potential curves for initial and final vibrational motion, and at low energies it helps put the total energy above the threshold and thus determines v_{\min} in Eq. (1).

The cross section (2) is completely determined when the potential energy curves V_i and V_f are specified including the width Γ_a of the latter, which is a resonance or autoionizing state. Since V_i , the ground state curve for O_2 is well known,⁴ it is necessary only to know the final curve V_f together with its width Γ_a in order to determine the entire family of cross sections given by (2). Accordingly, the procedure adopted in the present work was to parametrize this potential curve and its width. The parameters are then chosen with a view to fitting the experimentally determined $\sigma(T,E)$, in particular as given by Ref. 1, to the extent that this is possible. The curve V_f is first expanded in a series about $R_0 = 1.21 \text{ \AA}$ (the O_2 equilibrium distance), as

$$V_f(R) = E_0 - V' \Delta R + \frac{1}{2} V'' \Delta R^2 - (1/6) V''' \Delta R^3 \quad (4)$$

where $\Delta R = R - R_0$. For this width, we may either parametrize $\Gamma_a(R)$ and then derive ρ from Eq. (3) or a more exact formula, or else parametrize $\rho(R)$ directly and derive Γ_a . The latter course proved easiest, and was done in the form

$$\rho(R) = \rho' (R_c - R)^n \quad (R \leq R_c) \quad (5)$$

³ J. N. Bardsley, A. Herzenberg, and F. Mandl, Atomic Collision Processes (M.R.C. McDowell, ed.), North Holland, Amsterdam, 1964, p. 415.

⁴ F. R. Filmore, J. Quant. Spectry. Rad. Trans. 5, 369 (1965).

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and $\rho = 0$ beyond R_c . Lest the form of (5) appear arbitrary, this is actually the exact form which follows from (3) in the limit that the potential curve V_f is approximately linear between R_E and R_c and Γ_a has its threshold behavior $\Gamma_a \propto (R_c - R)^{L+1/2}$, where L is the electron's asymptotic angular momentum. In this case n would be equal to $L + 1$. However, the present results cover a wider range and so (5) represents simply a 3-parameter approximation to the true behavior. R_c is interpreted as the crossing point between V_f and the target potential curve into which it autoionizes, which is where the partial autoionization width $\Gamma_{a,j}$ and therefore its contribution to ρ goes to zero in the Born-Oppenheimer approximation.

It was found that the best fit to the experimental results¹ was obtained with the parameters in (4) and (5) chosen as follows:

$$E_0 = 7.8 \pm 0.2 \text{ eV}, \quad v' = 27 \pm 2 \text{ eV/\AA}, \quad v'' = 110 \pm 20 \text{ eV/\AA}^2, \\ v''' = 300 \pm 100 \text{ eV/\AA}^3 \quad (6)$$

and

$$n = 1.5 \pm 0.5, \quad \rho' = 41 \pm 3 \text{ \AA}^{-3/2}, \quad R_c = 1.44 \pm 0.03 \text{ \AA}. \quad (7)$$

The uncertainties expressed for the various quantities are meant to indicate the sensitivity of the fit to the various parameters, and do not necessarily reflect any judgment as to absolute errors.

The resulting cross sections at 300 and at 2100°K are plotted in Fig. 1 together with the experimental results at these temperatures. The theoretical curve for 3000° is also shown. The normalization of the 300° cross section was taken mainly from the work of Schulz.⁵ The theoretical curves in Fig. 1 have been averaged over a broad distribution of electron energies chosen to approximate that employed in the experiment

$$\sigma_{av}(T,E) = \int dE' f(E') \sigma(T,E') \quad (8)$$

⁵ G. J. Schulz, Phys. Rev. 128, 178 (1962). See also D. Rapp and D. D. Briglia, J. Chem. Phys. 43, 1480 (1965).

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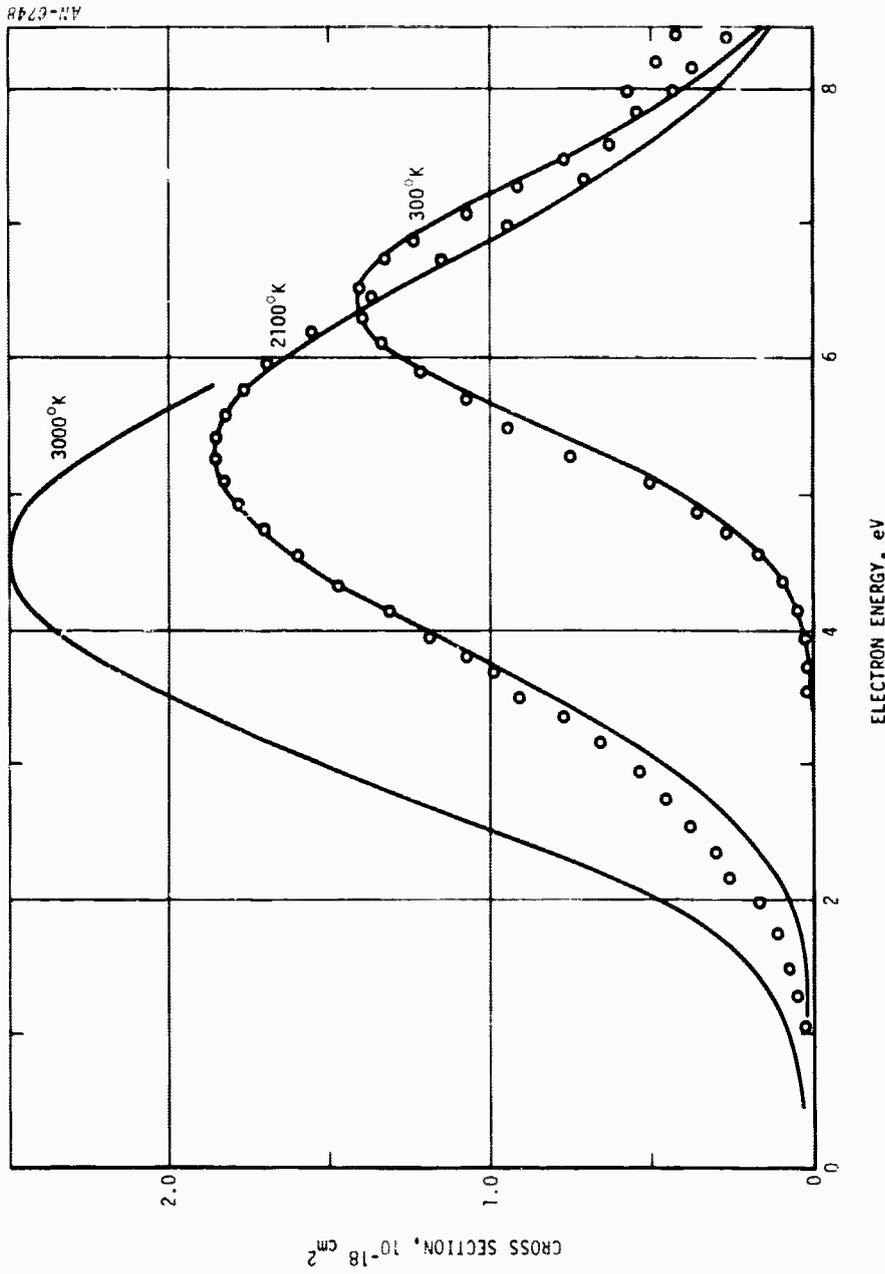


Figure 1. Dissociative attachment cross sections at 2100 and 300°K. The solid curves are from the present calculation with a broad electron spread included. The circles are the experimental points of Fite et al., normalized to the result of Ref. 5. The experimental 2100°K curve has been normalized to the present calculation, as discussed in the text. The theoretical curve for 3000° is also shown.

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where the electron distribution function $f(E')$ was taken to be a shifted Maxwellian corresponding to about 2860°K . The experimental 2100° cross section represents the experimental signal normalized to agree in magnitude with the presently calculated 2100° cross section, which is 1.3 times as large as that at room temperature. Though the magnitude of the cross section (as opposed to the signal) is not given explicitly in Ref. 1, the ratio of 1.3 found here is consistent with the cross sections implied by the discussion in these papers.

The theoretical fit to the experiments may be seen from Fig. 1 to be good, except that it fails somewhat below at the lowest electron energies. The experimental plateau above 8 eV is apparently due to some other cause. In Table 1, the calculated cross sections $\sigma(T,E)$ are tabulated for a number of temperatures. Note that unlike Fig. 1, these are not averaged over the electron distribution of Eq. (8).

In the course of the fitting process, it was found that the three parameters E_0 , V' and V'' of the potential curve V_f are essentially determined by the room temperature data, except that E_0 is raised by the presence of e^{-D} . The quantity V''' does not affect the 300° result and was chosen mainly for its influence on $D(E)$ (see Table 2). The expansion (4) of V_f should hold till roughly $R = 1.55 \text{ \AA}$.

The final state potential curve V_f for the system O_2^{-*} is shown in Fig. 2, together with other relevant states of O_2 and O_2^- taken from Gilmore's curves.⁴ It is believed that this potential curve together with the approximation (5) and (7) to the width (see also footnote 6) constitute a significant by-product of the present work. Note that the curve

⁶ Strictly speaking, one should put at least two terms like (5) into ρ , one for each set of states. This was tried and found to give essentially the same cross sections. The parameters were found very roughly to be (with $n = 1.5$) $R_{C1} = 1.52$, $\rho'_1 = 16$; $R_{C2} = 1.39$, $\rho'_2 = 27$. This gives approximately $\Gamma_1 = 1.5 (1.52-R)$ and $\Gamma_2 = 2.6 (1.39-R)$, while $\Gamma_X \approx 0.6 \Gamma_1$. However, the relative magnitude of ρ_1 and ρ_2 was found to be somewhat arbitrary without additional experimental information.

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TABLE 1

Dissociative attachment cross sections $\sigma(T,E)$ from Eq. (1) at various temperatures, in units of 10^{-21} cm^2 . The electron energy E is in eV and T in $^{\circ}\text{K}$. A sharply defined electron energy is assumed.

E/T	2600 $^{\circ}$	2200 $^{\circ}$	1800 $^{\circ}$	1400 $^{\circ}$	300 $^{\circ}$
1.0	5	1	0	0	0
1.5	22	4	0	0	0
2.0	98	27	4	0	0
2.5	312	119	29	3	0
3.0	650	306	104	20	0
3.5	1070	610	271	77	0
4.0	1530	1010	560	224	1
4.5	1920	1430	940	500	21
5.0	2120	1750	1340	890	155
5.5	2070	1870	1610	1280	520
6.0	1810	1750	1650	1500	1040
6.5	1420	1440	1450	1440	1380
7.0	1000	1050	1100	1160	1310
7.5	630	670	720	770	930
8.0	360	381	405	434	520
8.5	183	190	197	206	229
9.0	82	83	83	83	83

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TABLE 2

Table of activation energies, $D(E)$, experimental and theoretical
in eV, given in different approximation. D 's are in eV.

D_{av} comes from σ_{av} of Eq. (8), i.e., with electron spread.

D corresponds to σ with no electron spread.

C is the corresponding coefficient from Eq. (10)

in units of 10^{-18} cm^2 .

D_v was compared with rotation entirely neglected (vibration only).

E	D _{exp}	D _{av}	D	D _v	C(E)
1.0	--	1.59	2.43	2.61	370
1.5	--	1.36	2.05	2.12	280
2.0	1.0	1.14	1.64	1.66	200
2.5	.92	.93	1.18	1.18	72
3.0	.79	.72	.89	.91	39
3.5	.58	.55	.67	.68	23
3.75	--	.47	.59	.58	19
4.00	.29	.40	.50	.50	15
4.25	--	.34	.42	.42	12
4.50	.15	.28	.35	.35	10
4.75	--	.22	.28	.28	8

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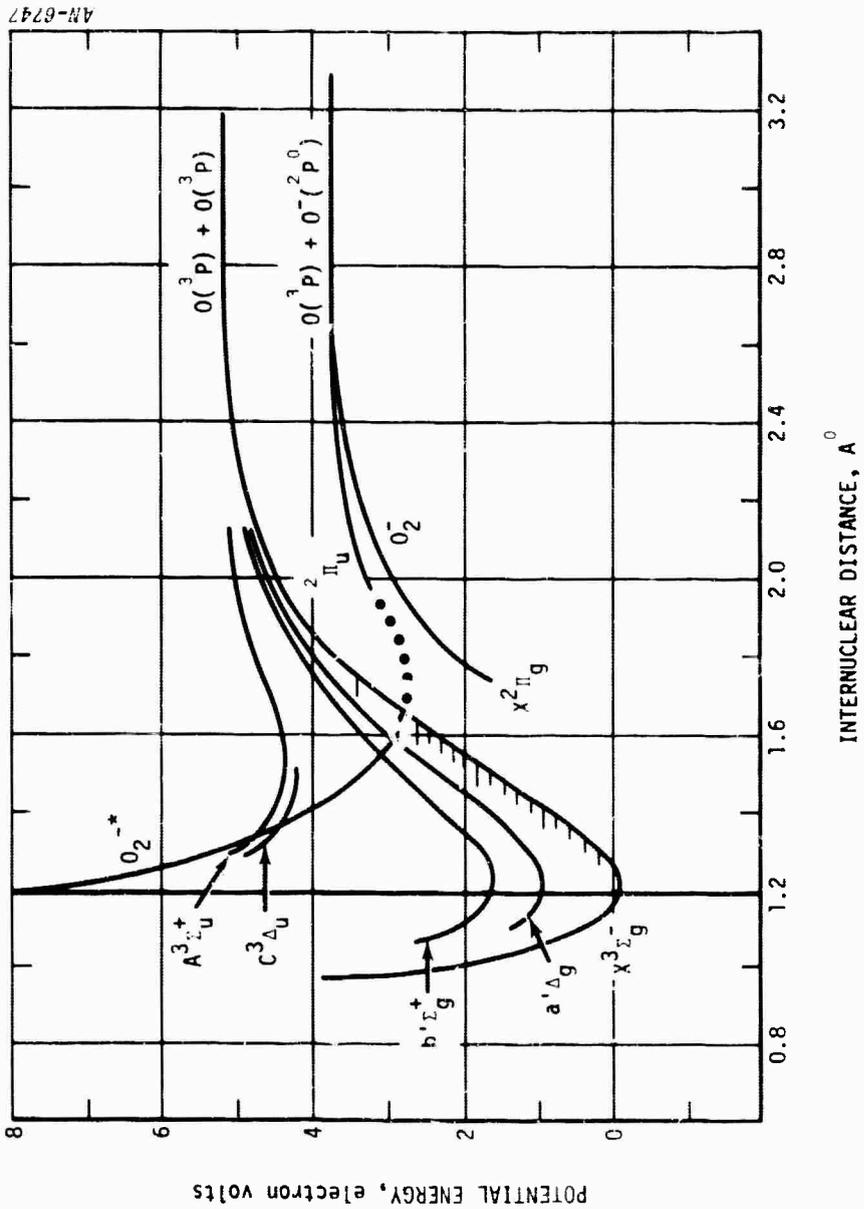


Figure 2. Potential energy curves for the O_2^- and O_2 system. The result of the present calculation, labeled O_2^- is shown in relation to the pertinent O_2 curves (from Ref. 4). The dotted portion of the curve is an extrapolation and shows schematically how the O_2^- curve is assumed to connect with the known portion of the Π_u curve.

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goes below the dissociation limit at about $R = 1.44 \text{ \AA}$ and becomes attractive. The dotted line from about $R = 1.55$ to 2.1 \AA represents the way in which this curve is assumed to connect up with the known asymptotic form of the ${}^2\Pi_u$ curve for O_2^{-*} . Although no use is made of this dotted region of the curve, the ${}^2\Pi_u$ configuration is fully consistent with the assumed electronic structure of the state, which would consist of an electron attached loosely to a combination A and C core. It follows that this state probably has a dissociation energy of the order of $1 \pm \frac{1}{2} \text{ eV}$.

The heuristics of choosing the parameters for ρ in (7) may be of interest. They were chosen to fit the 2100° cross section. The primary feature, namely the shift of the peak by 1 eV, was easily reproduced by simply varying the amplitude ρ' . However, the obvious choice of $n = 1/2$ (corresponding to a constant Γ_a) gave a cross section that was either nearly square in shape or double-peaked, depending on R_c . It was only when n was varied to between 1 and 2 that bell-shaped curves resulted. The value of 1.5 which fits best is gratifyingly close to the assumed correct threshold value, which as mentioned would give $n = 2$. Finally, fitting the observed cross section with fixed R_c loosely at $1.44 \pm 0.03 \text{ \AA}$. The value 1.44 for R_c was a little surprising. Reference to Fig. 2 shows that this lies squarely between the crossing of the A,C system at $R < 1.39$ and the crossing of the χ, a, b states at $R \geq 1.55$. R_c had been expected to coincide with one or the other of these crossings. The intermediate value, somewhat closer to A and C, is interpreted as meaning that there is considerable autoionization to all of the 5 allowed states, with the largest part going to A and C. The value of 1.44 is therefore taken as an average or compromise value.⁶

The foregoing results, (6) and (7), were derived with the cross sections arbitrarily normalized. Taking the 300° normalization of $1.4 \times 10^{-18} \text{ cm}^2$ from Ref. 5 allows $\Gamma_{a,\chi}$ in (2) to be determined. First, assuming the O_2^- state to be ${}^2\Pi_u$, it follows that the weighting factor g equals $2/3$. Further, it follows from $n = 1.5$ in (7) that the width Γ_a is roughly linear in electron energy. Substituting all this into Eq. (2) with $v = 0$ and ϵ

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small yields for the partial capture width from the state X

$$\Gamma_{a,X} = 0.034 E \quad (9)$$

This was incorporated in Fig. 1 and Table 1. The total width, Γ_a , also can be computed² from ρ as determined by (5) and (7). As Γ_a is not used directly, this was done only roughly, in a linear approximation, with the result $\Gamma_a(R) \approx 4(1.44 - R)$. Near the cross section peak then $\Gamma_{a,X}$ is somewhat more than 1/4 of Γ_a , which is also believable.

An analysis of the physical content of the calculation is made in Fig. 3, where the 2100° cross section is plotted in five successive approximations. In curve a, we set $v = r = \rho = 0$. This would correspond to the low temperature cross section without ρ . Including excited vibrational states in (b) broadens the curve considerably. Applying the rapidly varying survival factor $e^{-\rho}$ shifts (b) to (c), while the narrower curve a is shifted only to c'. (Differences in magnitude are suppressed in Fig. 3.) To a good approximation for O_2 , the difference between c and c' represents the entire temperature effect.⁷ If $\rho(E)$ or its energy variation were small, as for some other molecules, then the curves a and b would describe the effect and there would be broadening but no shift. Curves d and e, representing σ and σ_{av} respectively, show the modest shift caused by rotational states (agreeing with the analysis of Ref. 2) and the shift and tailing effect of a broad electron distribution. It can be seen from (d) that excited rotational states are of negligible importance compared to vibrational states.

Figure 4 analyzes the calculation from a slightly different point of view. The cross sections σ_v for attachment from the vth state are plotted individually. (The small dependence on r is here suppressed.) For each increase in v, there is a large shift to the left and a substantial increase in magnitude (σ_5 is 20 times as large as σ_0). Note that each cross section is cut off below its threshold ($E + E_v = 3.6$ eV). These curves show graphically the basis for the observed shift and the large low energy tail.

⁷ This is in agreement with the qualitative suggestion of Y. N. Demkov, Phys. Letters 15, 235 (1965). See also Ref. 2.

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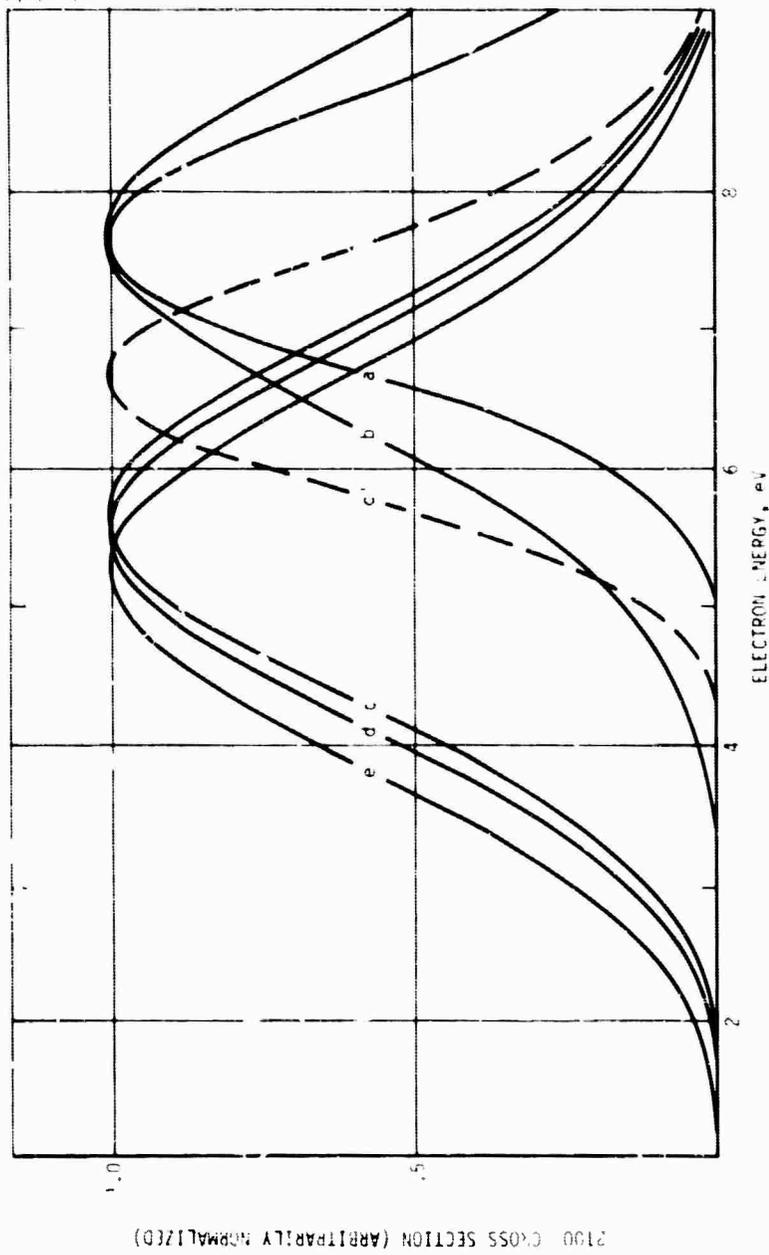


Figure 3. The 2100° attachment cross section in successive approximations, all arbitrarily normalized. In a, $v = r = \rho = 0$. Curve b includes excited vibrational states. In c, the factor $e^{-\rho}$ is also included. (Curve c' is curve a times $e^{-\rho}$. This is essentially the room temperature cross section, to be compared with c.) In d, rotation is included, giving σ of Eq. (1). Curve e is σ_{av} of Eq. (8), with a broad electron spread. If drawn to scale, curves a and b would be nearly two orders of magnitude larger than the others.

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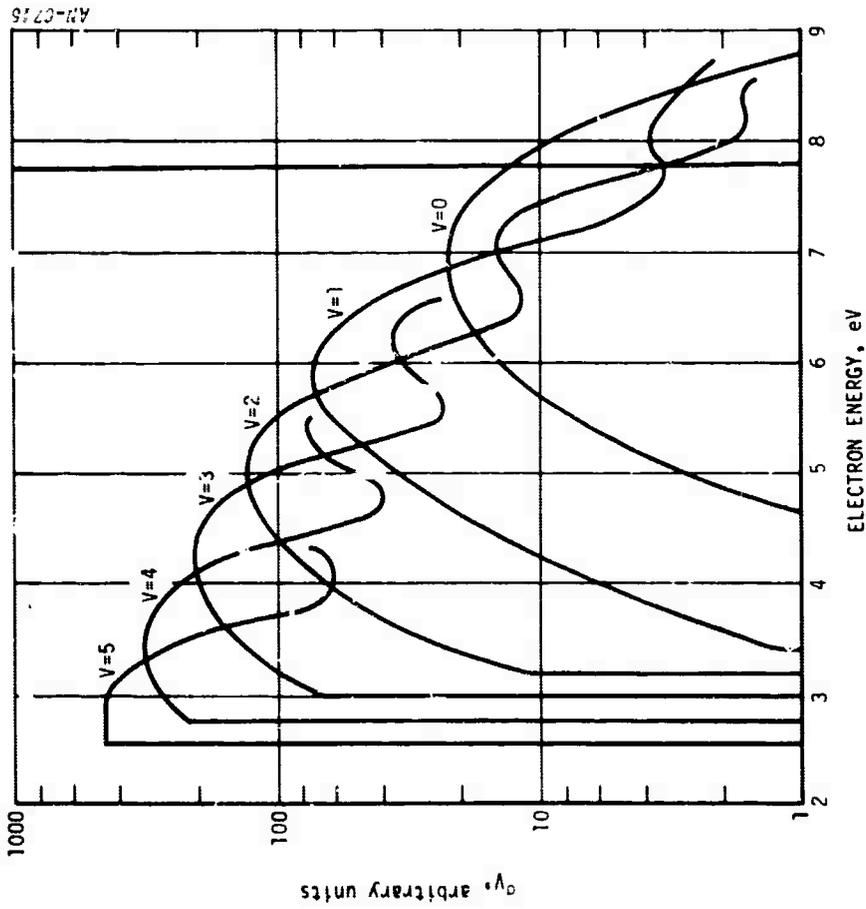


Figure 4. Cross Sections σ_v for attachment from the v th vibrational state, plotted against energy for $v = 0$ through 5. The lack of symmetry about the vertical line (7.8 eV) and the increase in magnitude with increasing v is due to the variation of the survival factor $e^{-\rho}$ with electron energy. A Boltzmann average of these cross sections (including higher v 's) reproduces the observed temperature dependence of the cross section $\sigma(T, E)$.

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A very interesting aspect of the work of Fite et al. was the finding that at the lower energies ($E \lesssim 5$ eV and $T \gtrsim 1000^\circ\text{K}$) the cross sections follow very closely the formula

$$\sigma(T,E) = C(E) e^{-D(E)/kT} \quad (10)$$

Exactly the same was found for the presently computed results. In Fig. 5, $\log \sigma$ is plotted against $1/T$ and the data are seen to lie on straight lines from roughly 800 to 3000°K . The slopes, $D(E)$, which were called activation energies, have a clear interpretation in the present work. They are the average internal energy (vibrational plus rotational) of the molecule which maximizes the summand in Eq. (1), showing the internal states which contribute most strongly to the temperature-averaged cross section. In columns 1 and 2 of Table 2, the experimental values $D_{\text{exp}}(E)$ are compared with the theoretical values $D_{\text{av}}(E)$ taken from σ_{av} of Eq. (8). The agreement is seen to be within 0.1 eV everywhere. (Probably the discrepancy at the largest E 's would be reduced if the experimenters had plotted σ rather than the uncorrected current.) The third column shows $D(E)$, the present result with sharply defined electron energies from Eq. (1). The very large difference between D and D_{av} is due to the tailing effect of the broad electron distribution. In the fifth column, the corresponding coefficient $C(E)$ from Eq. (6) is listed. The fourth column, labeled D_{v} , was calculated with vibrational states only (no rotational excitation). This corresponds to the data plotted in Fig. 6, which differs very little from Fig. 5. The difference between D and D_{v} is some measure of the relative importance of rotation, which seems to be very small except below about 2 eV. This is in disagreement with the assessment of Fite et al.¹ In this connection, it was found that at 2100° rotational states with $E_r \gg kT$ never contributed significantly to the sum in Eq. (1) (unlike the situation with the vibrational states), until E fell below about 2 eV. Even at the lowest energy of 1.0 eV the average excitation of the rotational states contributing to (1) was not much more than 20% of that of the average vibrational state ($v \approx 13$).

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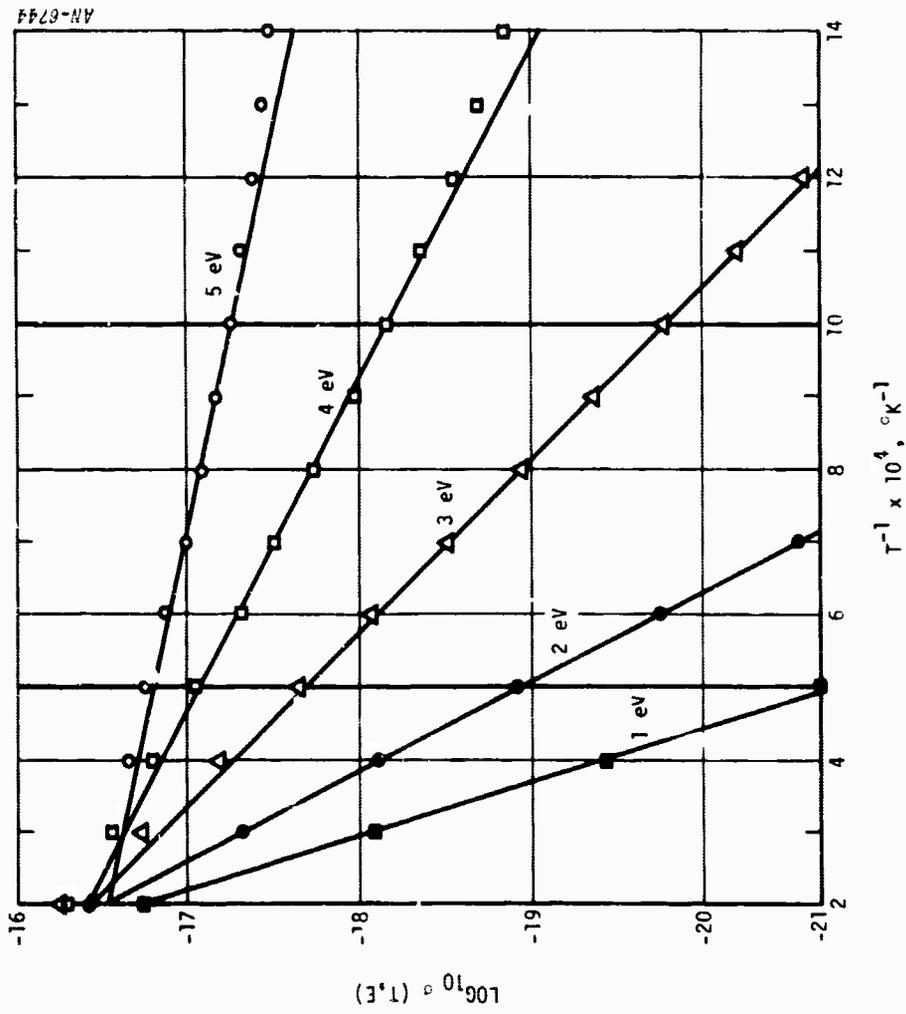


Figure 5. $\text{Log } \sigma(T, E)$ from the present calculation is plotted vs $1/T$ for various electron energies of 5 eV and below. The empirical formula (10) represents straight lines on this plot. Like the experimental results, which were plotted in the temperature region between the vertical straight lines, the calculated results also fall on straight lines. See text for discussion.

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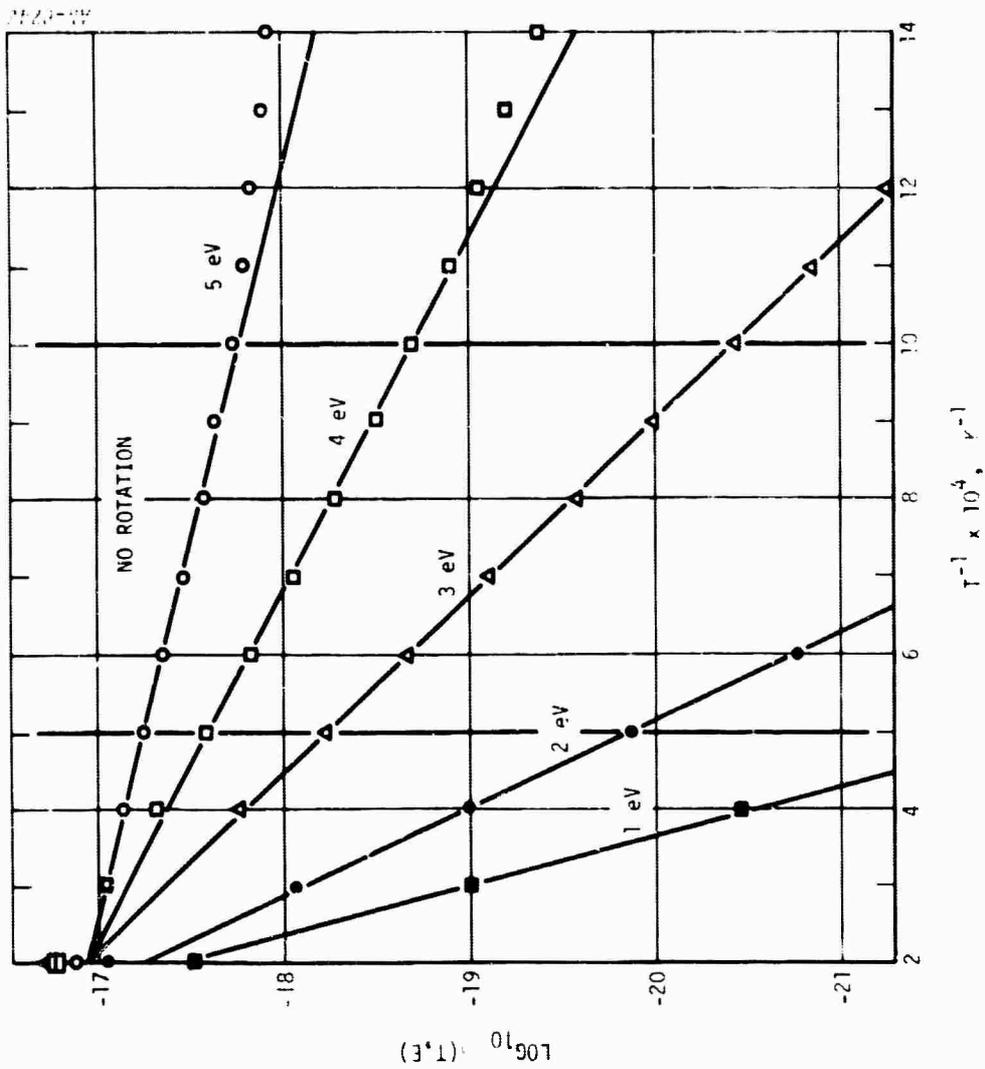


Figure 6. The same as Fig. 5 but from a calculation done without excited rotational states. The straight line behavior indicates that the relation given by Eq. (10) does not necessarily depend on rotational excitation.

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It is interesting in Table 2 that for electron energies well below the threshold of 3.6 eV, the values of $D(E)$ (not D_{av}) converge more or less to $3.6-E$, the internal energy necessary to raise the system above the threshold.⁸ This would indicate that the results for very high vibrational states are no longer sensitive to the details of the wave functions, but that these may be replaced by a suitable average value, in the statistical spirit. Thus, the simple concept of an activation energy does become appropriate in this limit. It seems, however, that at the very lowest energies (below 2 eV) the dynamical effects of rotation tend to bring $D(E)$ (as opposed to D_v) below the simple threshold value of $3.6-E$.

Finally, the consequences of the present analysis for processes other than dissociative attachment should be pointed out. Consider only the low temperature cross section for simplicity. The accepted interpretation³ of Eq. (2) is that the DA cross section is equal to a capture cross section to the state V_f of O_2^{-*} times $e^{-\rho}$, the chance of surviving to dissociate before autoionizing to some vibrational level of one of the five lowest O_2 states. Given the presently determined parameters (6) and (7), it follows that the capture cross section $e^{+\rho} \sigma_{DA}$ is roughly 70 times that for DA, with a peak value of about $1.0 \times 10^{-16} \text{ cm}^2$ at 7.8 eV. From $R_c = 1.44$ we would expect that at least half⁹ of this capture cross section will decay to the states A and/or C, resulting in dissociation, while the remainder autoionizes to the states X, a and b, (about half of it to X), resulting in excitation of most of the vibrational levels of these states. Whether the contribution of this to the respective cross sections is significant is not clear at present.

⁸ This relation was obtained previously by M. A. Fineman from similar experiments done by J. W. McGowan. (Private communication.)

⁹ See also Footnote 6.

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QUASI-ADIABATIC MOLECULAR STATES: AN ALTERNATIVE TO THE NON-CROSSING RULE*

by

Thomas F. O'Malley

ABSTRACT

Because of the non-crossing rule, the conventional definition of adiabatic states has been increasingly regarded as unsuitable for describing collisions. An alternative definition based on a generalization of the resonance is given, defining states which may cross freely. As an immediate application, these states tend to resolve a serious discrepancy in the interpretation of recent He_2^+ recombination data.

The non-crossing rule (NCR) of von Neuman and Wigner¹ which states that molecular states of the same symmetry cannot cross, has been a source of growing dissatisfaction² to many molecular physicists interested in atomic collisions and reactions. Nevertheless it has been accepted, although sometimes reluctantly, as the apparent price that one must pay for having an "adiabatic" definition of electronic states, i.e., a definition in which the internuclear coordinate R is held temporarily fixed. It is the purpose of the present note to point out that there exists an accept-

* Submitted to Phys. Rev. letters.

¹ J. Von Neumann and E. P. Wigner, Phys. Zeits. 30, 467 (1929).

² See for example W. L. Lichten, Phys. Rev. 131, 229 (1963). Lichten's emphasis on the physical importance of certain pseudocrossing single configuration states is very much in the spirit of the present work. These states would be a first rough approximation to the ϕ_r of the present paper. F. T. Smith, D. C. Lorents, W. Aberth and R. P. Marchi, Phys. Rev. Letters 15, 742 (1965) have been forced to assume similar crossing curves. See also W. R. Thorson and S. A. Boorstein, in IVth International Conference on the Physics of Electron and Atomic Collisions (Science Bookcrafters, Hastings, N.Y., 1964), p. 218.

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able and precise definition of adiabatic electronic states which are not constrained by an NCR and which, as a result, are able to approximate the physical states which are actually followed in various types of rearrangement collisions.

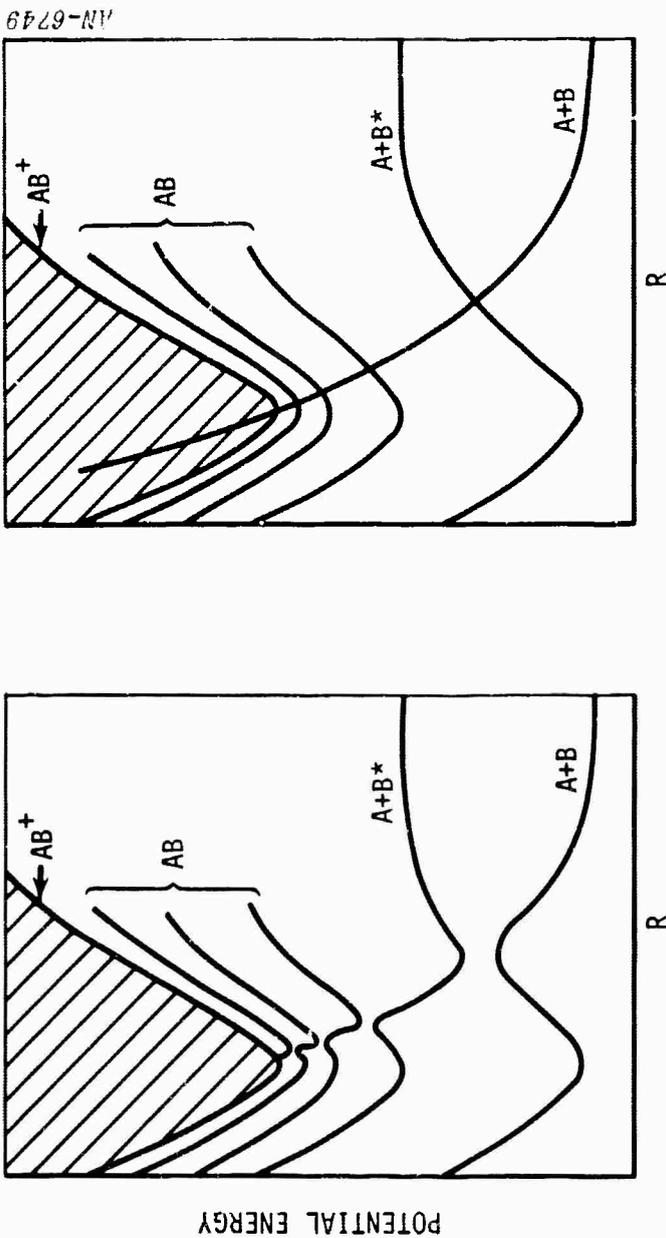
The simplest way of presenting the NCR is in terms of two approximate trial functions, ϕ_1 and ϕ_2 , supposedly representing different states of the same symmetry, whose approximate energy curves cross. In order to get an improved approximation, linear combinations of the original states are sought which diagonalize the 2×2 electronic Hamiltonian, H_{e1} . When this is done, the resulting new states ϕ_I and ϕ_{II} are known as "true adiabatic" states. The corresponding true adiabatic eigenvalues $E_I(R)$ and $E_{II}(R)$ are found to be separated by the amount $E_I - E_{II} = \left[(H_{11} - H_{22})^2 + 4H_{12}^2 \right]^{1/2}$, a positive definite quantity. In other words they cannot cross, and must behave in a way illustrated in Fig. 1(a). This in brief is the NCR.

In addition to NCR, there is a second and closely related logical consequence of defining true adiabatic states which was deduced by Massey.³ Massey's theorem in essence points out that, since by choice the true adiabatic states diagonalize H_{e1} , it follows that collision-induced transitions between electronic states cannot be mediated by a matrix element of the diagonal operator H_{e1} . Consequently these transitions must be caused by T' , the coupling kinetic energy term neglected in the Born-Oppenheimer approximation, and so this useful approximation must be abandoned when transitions occur. Logical and rigorous as it is, Massey's theorem, like NCR in its early days, has had difficulty of acceptance in that it seems to conflict with much of what is known of reactions, especially the theory of dissociative recombination⁴ and attachment.⁵ How misleading (though formally correct) these two theorems are when applied to collisions is

³ H.S.W. Massey, Negative Ions (Cambridge Univ. Press, N.Y., 1950).

⁴ D. R. Bates, Phys. Rev. 78, 492(L) (1950).

⁵ T. F. O'Malley, Phys. Rev. 150, 14 (1966).



(a)

(b)

Figure 1. Potential energy curves for a typical molecule AB, showing a series of states of the same symmetry, together with the ion AB^+ . In 1(a), the states are conventional true adiabatic states which must obey the non-crossing rule with the resultant avoided crossings and "obligatory humps". In 1(b), the state AB_r , defined as a quasi-adiabatic state (see text), is not bound by the non-crossing rule and cuts freely across the other discrete states and the continuum (shaded area) as well.

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brought home by the fact that even Massey⁶ was led in 1937 to conclude on their strength that dissociative recombination must necessarily be a very slow reaction. It was not until many years later⁷ that this was to some extent corrected.

We shall next point out very briefly, for those not already acquainted with them, some of the shortcomings of true adiabatic states and the consequent NCR when applied to collision problems. Then the alternative "quasi-adiabatic" states will be introduced, which have the property that they may cross freely and do not require non-adiabatic (T') coupling. These states should probably be used in connection with all problems involving collisions or dissociations.⁸

Many of the problems and distressing features of the NCR are illustrated with the help of Fig. 1(a) as contrasted with 1(b). The curves in Fig. 1(b) might be found, for example, when one first does a calculation with very simple Heitler-London or molecular orbital functions. A slightly more elaborate calculation, as described above, would give curves with the properties of true adiabatic states as shown in Fig. 1(a) with their avoided crossings and "obligatory humps."

Aside from the obvious aesthetic objections to the kind of curves in Fig. 1(a), there are a number of more practical drawbacks connected with these true adiabatic curves. First there is the fact if the colliding atoms have almost any finite velocity the probability of their actually following the true adiabatic curves as opposed to the crossing curves is known to become vanishingly small, as is indicated in the next paragraph. Next, the Born-Oppenheimer approximation, which is generally so very useful and accurate

⁶ H.S.W. Massey, Proc. Roy. Soc. A163, 542 (1937).

⁷ D. R. Bates and H.S.W. Massey, Proc. Roy. Soc. A187, 261 (1947).

⁸ Dissociation is here taken to mean the dissociation of repulsive states mainly, or predissociation by curve crossing. Predissociation by barrier tunnelling is another matter.

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for molecular states, breaks down completely in the neighborhood of an avoided crossing when one uses true adiabatic states. This follows from Massey's theorem. Finally, there are two large classes of collisions where theorists have long since been forced to abandon the NCR, at least for practical purposes, and to think in terms of the crossing curves in Fig.1(b).

The first class of collisions where the NCR has had to be suspended is the slow reactive or inelastic collisions between heavy particles which are well described in the low energy region by the Landau-Zener theory,⁹ together with subsequent improved versions. In deriving this theory, one starts with two "approximate" electronic states, which are never defined precisely, but whose physical interpretation is assumed to be clear. These states have potential curves which "pseudo-cross." The transition probability of passing from one of the pseudocrossing curves to the other is derived, after some approximations, and found to be $1 - e^{-2\delta}$ for each passage, where $\delta = \pi V^2/hv \Delta F$. (V is the energy of interaction between the crossing states, so that $2V$ would be the smallest separation of the true adiabatic states; v is the internuclear velocity and ΔF is the difference of slopes.) One consequence of the Landau-Zener formula, as mentioned above, is that for typical parameters the probability $1 - e^{-2\delta}$ of following the true adiabatic curve becomes negligible for almost any finite velocity. Now although this theory has been found to describe accurately all sorts of low energy reactions, it is still necessary to apologize for the "pseudocrossing" (which is essential to the derivation) and to point out that the true adiabatic curves of course cannot really cross. Perhaps of more practical concern is the fact that the pseudocrossing electronic states simply are not defined, except for being "sufficiently inaccurate" to allow them to cross. As better computer calculations become feasible, this shortcoming should become progressively more and more of a problem.

The second class of collisions, which cannot even be described conceptually in terms of the true adiabatic states and the NCR, consists of

⁹ L. Landau, *Physik. Z. Sowjetunion* 2, 46 (1932). C. Zener, *Proc. Roy. Soc.* A137, 696 (1932).

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the processes of dissociative recombination⁴ ($e + AB^+ \rightarrow AB_r \rightarrow A + B$), and dissociative attachment⁵ ($e + AB \rightarrow AB_r^- \rightarrow A + B^-$). (Fortunately, these processes, when properly analyzed, also point the way to the needed definition of "quasi-adiabatic states.") The recombination process is understood by reference to Fig. 1(b). An electron collides with the ion AB^+ , and causes an electronic transition to the state labeled $(AB)_r$, which state finally dissociates to $A + B$. It is seen that the curve $(AB)_r$, in coming in from $-\infty$, first had to violate NCR countless times and cross an entire Rydberg series of the same symmetry before reaching the curve AB^+ . More seriously, after crossing AB^+ and entering the hatched region (the electronic continuum of AB), the curve must then cut through a continuum of states, in flagrant violation of NCR. This latter situation is exactly the same for the closely related dissociative attachment process.⁵ Figure 1(a) is the way these curves would have had to be drawn had the NCR not been ignored.

Ironically the crossing of the continuum, which presents the strongest violation of NCR, also points the way to the solution of the entire non-crossing dilemma. For a discrete state like AB_r which is degenerate with (crosses) a continuum, is a familiar situation in theoretical physics and has been dealt with exhaustively.¹⁰ Such a discrete state is the "resonance" or "quasi-stationary state." It is by use of such states that the problem of dissociative attachment (and by inference recombination) has been successfully treated in a fully quantitative way.⁵

The definition of the resonance or quasi-stationary state for the autoionizing electronic states of molecules is discussed in some detail in Ref. 5 as well as elsewhere.¹¹ For the present purpose, the main features are as follows: The electronic wave function ϕ_r of the resonance state is artificially restricted in some way to a portion of Hilbert space by a pro-

¹⁰ H. Feshbach, *Ann. Phys. (New York)* **5**, 357 (1958); **19**, 287 (1962); and references to previous work therein contained.

¹¹ J. N. Bardsley, A. Herzenberg and F. Mandl, *Atomic Collision Processes* (N.R.C. McDowell, Ed.) North Holland, Amsterdam (1964), p. 415. J.C.Y. Chen, *J. Chem. Phys.* **40**, 3507 (1964).

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jection operator $Q^{(0)}$, while its energy eigenvalue

$$\langle Q^{(0)} \phi_r | H_{el} | Q^{(0)} \phi_r \rangle = \epsilon(R) \quad (1)$$

is made stationary. (As in any adiabatic definition, R appears parametrically.)

Having defined ϕ_r , a new projection operator, $Q = \phi_r \langle \phi_r |$ is constructed which together with $P = 1 - Q$ decomposes the electronic Hamiltonian H_{el} as follows

$$H_{el} = \begin{bmatrix} PH_{el}P & PH_{el}Q \\ QH_{el}P & QH_{el}Q \end{bmatrix} \quad (2)$$

The eigenstate corresponding to $PH_{el}P$, called ϕ_p the "potential scattering" state, is constrained by P to be orthogonal to ϕ_r . The above decomposition of H_{el} , or more properly of the full H , formed the basis of the new formal theory of rearrangement collisions introduced in Ref. 5.

The two states ϕ_r and ϕ_p have been defined to lie in orthogonal portions of Hilbert space and they leave H_{el} undiagonalized (note that it is only the full H which must be diagonal). One consequence of a non-diagonal H_{el} is that transitions from ϕ_p to ϕ_r may be caused by the off-diagonal electronic matrix element $PH_{el}Q$, in contrast to the Massey theorem. Thus the coupling term T' is no more important here than in ordinary molecular states and the usefulness of the Born-Oppenheimer approximation is preserved. More important, and in fact paramount in the present treatment, the mathematically orthogonal and physically distinct states ϕ_r and ϕ_p are not now combined as were the states of von Neumann and Wigner, into "true adiabatic" states of H_{el} , resulting in the NCR. Rather they are allowed to serve as a convenient starting point for an exact solution of the collision problem. (This theory will be published elsewhere.) By thus preserving their identity, the energies E_p and E_r of these states are not constrained to avoid

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crossing, and the levels can and do cross. The lack of a prohibition against crossing may perhaps be made clear by noting that as eigenvalues of different Hamiltonians, PHP and QHQ, the two levels are entirely independent of one another.

What has been said so far of the quasi-stationary states ϕ_r and ϕ_p has referred explicitly to the hatched region of Fig.1(b), i.e., to the region where the state AB_r , with wave function ϕ_r , is autoionizing. It is the burden of this paper to point out that all the difficulties resulting from true adiabatic states, i.e., the NCR and the Massey theorem, are avoided if only one uses exactly the same definition of states (with exactly the same projection operators $Q^{(o)}$ and Q) for all R even after the state AB_r has fallen below the continuum and can no longer autoionize. It is not necessary to make any changes at all in the discrete region. Again the quasi-stationary state ϕ_r is defined with the same projection operator $Q^{(o)}$. The resulting new projection operator P is then used to define the orthogonal "potential scattering" function ϕ_p . Again the corresponding potential curves ϵ_r and ϵ_p are not constrained by the NCR or by Massey's theorem. The only minor difference is that the name "potential scattering" function is no longer very appropriate, since ϕ_p is now a discrete quasistationary state, on the same footing with ϕ_r .

The name which is suggested for the crossing states ϕ_r and ϕ_p , defined as above and extended to the discrete region, is quasi-adiabatic states, short for quasi-stationary adiabatic states. This is appropriate since they are adiabatic, being defined with R fixed, but unlike the "true adiabatic" states they are only quasi or artificial bound states.

To avoid possible misunderstanding, something should be said here about what is presently meant and not meant by the projection operator $Q^{(o)}$. The obvious definition of this projection operator and presumably the most useful is that of Feshbach,¹⁰ which defines a state in which an electron is bound to an excited core. However, $Q^{(o)}$ is meant to be somewhat more flexible. For one thing, certain simplifications of Feshbach's states may be

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desirable.¹² In general, any artificial restraint on the wave function which leads to a physically meaningful and useful state is considered to be included as a possible $Q^{(0)}$ since this may always be thought of as being produced by some kind of projection operator. As one example, an artificial constraint might sometimes be useful for defining ionic states. However, at present, only the Feshbach type of core excited state is actually envisaged.

There are a number of examples in the literature of states which have been defined in such a way that they happen to satisfy the definition of quasi-adiabatic states. Two of these will be mentioned. First, there is the $(\sigma_u 1s)^2 1\Sigma_g$ state of H_2 , as calculated with the simplest single configuration wave function.¹³ This configuration $(\sigma_u 1s)^2$ satisfies the definition of the lowest Feshbach-type resonance in the H_2 system, and so is a quasi-adiabatic state. The potential curve of this state has been plotted as an illustration in Ref. 13. As expected, it cuts right across higher states of the same symmetry, crosses the entire Rydberg series and ultimately becomes autoionizing, just as AB_r of Fig 1(b). An interesting incidental feature of the curve is that it becomes ionic at large R . Naturally, as more ambitious calculations have been made, looking for true adiabatic states, this state has been mixed with others, resulting in humps and avoided crossings as in Fig. 1(a).

A second example of quasi-adiabatic electronic states in the literature is seen in the He_2 states found by Mulliken¹⁴ and labeled B Core states. These included the $B2s 3\Sigma_g^+$, and a $B3p 3\Sigma_u^+$ state. The concept of B Core state, as pointed out in Ref. 4, directly satisfies Feshbach's definition of a resonance state. Consequently we expect first that these states should

¹² See for example L. Lipsky and A. Russek, Phys. Rev. 142, 59 (1966).

¹³ W. Kauzmann, Quantum Chemistry (Academic Press, New York, 1957), p. 397.

¹⁴ R. S. Mulliken, Phys. Rev. 136, A962 (1964).

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be autoionizing for small R , and in fact they are. Further, as R increases they should cut through the Rydberg series of the same symmetry, which they also do. However, both of these curves have been drawn in Ref. 14 so as to avoid crossing the lowest state of the series (${}^3\Sigma_g^+$ and ${}^3\Sigma_u^+$) and so they both turn up sharply above $R = 2a_0$, somewhat in the fashion of Fig. 1(a). It is suggested here that if the definition of quasi-adiabatic state, implied by the B Core definition, is applied consistently, then these states need not avoid crossing even the lowest states in the series, but it is possible that they would simply decrease monotonically with R as the AB_r curve of Fig. 1(b), and dissociate into the lowest 3S and 3P state of He respectively.

This last suggestion would tend to remove the discrepancy which presently exists between these curves of Mulliken and subsequent results of Robertson.¹⁵ The latter observed a state of the system which is autoionizing at small R and which dissociates into the lowest 3P state of He in apparent disagreement with Mulliken's curves. But if the definition of quasi-adiabatic B core states is adopted as is here suggested, then for any given states of the dissociation products (and in particular for those found by Robertson) there ought to be a corresponding molecular curve satisfying the definition of a B core quasi-adiabatic state. This curve would be expected to be purely repulsive, following the shape of the B core, and at smaller R to cross the Rydberg series and become autoionizing. Thus, the existence of a suitable potential curve, corresponding to Robinson's data, should present no problem once the artificial restraints imposed by NCR are removed by using quasi-adiabatic states. It is not clear at present whether this particular state might be the ${}^3\Sigma_u$ curve of Mulliken, redrawn to join B ${}^3\Sigma_u$, or perhaps a ${}^3\Pi_u$ B core state, similarly redrawn.

In summary, a definition has been given of quasi-adiabatic states which it is proposed should replace the conventional true adiabatic states for all processes involving collisions or dissociations.⁸ In particular, it was shown that such states have the advantage of not being burdened by a non-crossing rule, so that they may reproduce the curves that are actually followed in a physical collision or dissociation. Further, they do not

¹⁵ W. W. Robertson, J. Chem. Phys. 42, 2064 (1965); C. B. Collins and W. W. Robertson, J. Chem. Phys. 43, 4188 (1965).

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satisfy Massey's theorem, so that the Born-Oppenheimer approximation may be retained. These states may be of most immediate usefulness in connection with the semi-empirical process of constructing potential curves to fit or explain given experimental data. An improved theory of heavy particle collisions based on these states will be published elsewhere.

Finally, these states are not meant to replace the conventional true adiabatic states in those areas where the latter are actually useful, namely where such states are either very widely separated or parallel and where in addition the discrete vibrational level of interest is sufficiently low so that the Landau-Zener exponent δ would be very large.

Thanks are due B. A. Lippmann and P. J. Redmond for stimulating discussions.

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THEORY OF RESONANT DISSOCIATIVE RECOMBINATION*

by

Peter J. Redmond

The theory is developed with particular emphasis on the interaction of the resonant state and the infinite set of Rydberg states crossed by the resonant state. It is shown that the interaction is large only for a finite subset of the Rydberg states.

In this paper we consider the process $e^- + AB^+ \rightarrow A + B$ where the atoms in the final state will generally be excited. We shall show that the total cross section corresponding to a sum over all possible exit channels can be calculated in a fairly straightforward way. In principle the theory also permits the calculation of branching ratios although such a calculation would be much more involved.

We assume that the reaction proceeds by the formation of a resonant complex AB^* so that $e^- + AB^+ \rightarrow (AB)^* \rightarrow A + B$. It is well known that there are an infinity of such resonant states lying below the first electronically excited state of the AB^+ system. It is also known that the widths of the resonant states are small compared to the spacing of the resonant states so that they are excited independently. However, when the atoms A and B separate they move along a potential curve which must cross (or "pseudo cross") an infinite Rydberg series of states. These curve crossings may lead to a coupling between the resonant states and will lead to a distribution of the particles over a variety of exit channels. It is this latter phenomena which makes the theory of dissociative recombination more complicated than the theory of dissociative attachment. We shall show that only

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a finite (and usually small) number of the resonant states can be coupled in this fashion and that the coupling can be described by an energy dependent matrix for a reflection amplitude.

The wave function for the system may be written in the form

$$\begin{aligned} \psi(\underset{\sim}{R}, \underset{\sim}{\rho}, \underset{\sim}{k}) = & \sum_{\lambda} A(\lambda, \underset{\sim}{R}) \phi(\lambda, \underset{\sim}{R}, \underset{\sim}{\rho}) \\ & + B_0(\underset{\sim}{R}) \chi_0^{(+)}(\underset{\sim}{R}, \underset{\sim}{\rho}, \underset{\sim}{k}) \\ & + \int d\underset{\sim}{k}' \sum_j B(\underset{\sim}{j}, \underset{\sim}{k}', \underset{\sim}{R}) \chi^{(-)}(\underset{\sim}{j}, \underset{\sim}{k}', \underset{\sim}{R}, \underset{\sim}{\rho}) \end{aligned} \quad (1)$$

where $\underset{\sim}{R}$ is the nuclear separation and $\underset{\sim}{\rho}$ represents the electronic coordinates. The wave functions $\phi(\lambda)$ are the electronic wave functions for the resonant states.¹ The χ are the electronic scattering states and it is assumed that they diagonalize the electronic part of the Hamiltonian in the subspace of states orthogonal to the $\phi(\lambda)$. The $\chi^{(+)}$ satisfy incoming boundary conditions and the χ^{-} outgoing conditions and the vector $\underset{\sim}{k}$ represents the momentum of the incoming or outgoing electron. The term $B_0 \chi^{(+)}$ is the incoming wave and B_0 is the nuclear wave function of the initial AB^+ state. The states $\phi(\lambda)$ and χ are slowly varying functions of the nuclear separation. This is possible only if the energy curves $E_{\lambda}(\underset{\sim}{R})$ corresponding to the $\phi(\lambda)$ are allowed to cross.

The only non-diagonal matrix elements of the electronic Hamiltonian are then

$$\langle \phi(\lambda, \underset{\sim}{R}), H_{el}, \chi^{(+)}(\underset{\sim}{j}, \underset{\sim}{k}', \underset{\sim}{R}) \rangle \equiv \gamma_{\lambda}(\lambda, \underset{\sim}{j}, \underset{\sim}{k}', \underset{\sim}{R}) \quad (2)$$

and

$$\langle \phi(\lambda, \underset{\sim}{R}), H_{el}, \phi(u, \underset{\sim}{R}) \rangle \equiv W(\lambda, u, \underset{\sim}{R}) \quad (3)$$

¹ We use the term resonant state to include all those discrete states of the neutral system which interact with the state initially excited.

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The γ and W are non-vanishing in separated regions of configuration space. The matrix element W is appreciable only in the immediate vicinity of a curve crossing whereas the γ 's are non-vanishing only when the resonant state curve lies above the ground state potential curve of AB^+ .

Since the ϕ and χ are slowly varying functions of R , the many state Born-Oppenheimer (adiabatic) approximation is appropriate and $(E-H)\psi = 0$ is equivalent to the set of coupled equations.

$$\begin{aligned} \left(E - E_\lambda(R) + \frac{1}{2M} \nabla^2 \right) A(\lambda, R) &= \gamma_+(\lambda, 0, k, R) B_0(R) \\ &+ \int dk' \sum_j B(j, k', R) \gamma_-(\lambda, j, k', R) \\ &+ \sum_\mu W(\lambda, \mu, R) A(\mu, R) \end{aligned} \quad (4)$$

and

$$\left(E - E_j(R) - \frac{k'^2}{2m} + \frac{1}{2M} \nabla^2 \right) B(j, k', R) = \sum_\lambda A(\lambda, R) \gamma_+^*(\lambda, j, k', R), \quad (5)$$

where m and M are the electronic and reduced atomic masses respectively.

The solution of Eq. (5) which satisfies the proper boundary conditions may be written asymptotically

$$B(j, k', R) = \frac{1}{E - E_j - \frac{k'^2}{2m} + \frac{1}{2M} \nabla^2 + i\epsilon} \sum_\lambda A(\lambda, R) \gamma_+^*(\lambda, j, k') \quad (6)$$

If the Green's function in Eq. (6) is expanded in terms of the eigenstates of the nuclear Hamiltonian, the discrete states describe elastic scattering and vibrational and rotational excitation. The continuum states contribute to dissociation although the main contribution to dissociation comes from the $A(\lambda, R)$ terms. For example, the elastic scattering comes from the term

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$$B_{\text{elastic}}(j, k', R) = \frac{B_0(R) \delta_{j,0}}{\frac{k^2}{2m} - \frac{k'^2}{2m} + i\epsilon} \sum_{\lambda} \int dR' B_0(R') A_{\lambda}(R') \gamma_{+}^{*}(\lambda, 0, k', R'). \quad (7)$$

This term interferes with the outgoing wave part of $B_0(R) \chi^{(+)}(0, k, R)$ to give a typical resonance pattern for the elastic scattering.

In order to determine the dissociative cross section we take the divergence of the heavy particle flux. We find

$$\begin{aligned} \nabla \cdot \left[\sum_{\lambda} (A^{*}(\lambda, R) \nabla A(\lambda, R) - A(\lambda, R) \nabla A^{*}(\lambda, R)) \right. \\ \left. + \sum_j \int dk' (B^{*}(j, k', R) \nabla B(j, k', R) - B(j, k', R) \nabla B^{*}(j, k', R)) \right] = \\ = \sum_{\lambda} (A^{*}(\lambda, R) \gamma_{+}(\lambda, 0, k, R) B_0(R) - A(\lambda, R) \gamma_{+}^{*}(\lambda, 0, k, R) B_0(R)) \quad (8) \end{aligned}$$

Since there is no incoming heavy particle flux the total cross section for dissociation can be obtained by integrating the right-hand side of Eq. (8) over all space. Because of the presence of the factor $B_0(R)$ on the right-hand side of Eq. (8) (and in the integral occurring in Eq. (7)), it is only necessary to determine the functions $A(\lambda, R)$ in the Franck-Condon region.

In determining $A(\lambda, R)$ it is necessary to consider two different possibilities. If the electron energy is sufficiently high so that all the attractive potential curves which are crossed by the resonant curve involved correspond to exit channels which are open, then any outgoing flux generated on the Franck-Condon region will remain outgoing. The

² T. F. O'Malley, Phys. Rev. 150, 14, 1966.

³ J. N. Bardsley, A. Herzenberg, and F. Mandl, Atomic Collision Processes, edited by M.R.C. McDowell (North Holland Publishing Co., Amsterdam 1964), p. 145.

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$A(\lambda, R)$ can then be determined in precisely the same way that O'Malley² and Mandl and Herzberg³ treated the dissociative attachment problem. The only difference is that the final formula in the recombination case corresponds to several exit channels instead of only one as in the attachment problem.

If some of the exit channels with attractive potential curves are closed, some of the outgoing flux generated in the Franck-Condon region will correspond to particles which are temporarily bound and return to the Franck-Condon region. The finite number of resonant states coupled to such exit channels will then be coupled to each other. These effects can be described by a finite reflection coefficient matrix which gives the amplitude of the reflected wave in any resonant state produced by an outgoing wave in another coupled resonant state. This matrix can be determined by using the Landau-Zener theory (or some variant of it) and considering the possible histories of outgoing particles.

The system $e^- + H_2^+ \rightarrow H + H$ provides a comparatively simple illustration of the various possibilities discussed above and the theory will be applied to the system at the meeting.

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FORMULATION OF THE TWO-STATE PROBLEM IN TERMS OF ADIABATIC POTENTIAL CURVES*

by

Peter J. Redmond

ABSTRACT

When two molecular adiabatic potential curves nearly cross, the electronic wave function is a rapidly varying function of the internuclear separation. The one-state Born-Oppenheimer approximation is then not valid. By introducing appropriate linear combinations of the two adiabatic states involved a two-state Born-Oppenheimer approximation can be made. The resulting pair of coupled equations for the nuclear wave function are identical with those obtained in the conventional two-state theories. However, all the parameters can be determined by an inspection of the adiabatic curves and the validity of the approximation scheme can be justified.

I. INTRODUCTION

In the usual approach to molecular problems, or to collision problems, one makes the adiabatic (Born-Oppenheimer)¹ approximation. The Hamiltonian is written as the sum of a nuclear kinetic energy term and an electronic Hamiltonian

$$H = \frac{1}{2M} \nabla_R^2 + H_{el}(R) \quad (1)$$

and the eigenstates of H_{el} are calculated

$$H_{el} \phi_\alpha(R, \xi) = E_\alpha(R) \phi_\alpha(R, \xi) \quad (2)$$

* Submitted to ARPA for publication clearance.

¹ M. Born and J. R. Oppenheimer, Ann der Phys 84, 457 (1927).

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The total wave function may be written as a linear combination of these electronic states with coefficients which are functions of the internuclear separation R ,

$$\psi = \sum_{\alpha} F_{\alpha}(R) \phi_{\alpha}(R, \xi) \quad (3)$$

The equation for $F_{\alpha}(R)$ is then

$$\left(-\frac{1}{2M} \nabla^2 + E_{\alpha}(R) - E \right) F_{\alpha}(R) = \sum_{\beta} \left(\frac{1}{M} \langle \phi_{\alpha}(R), \nabla \phi_{\beta}(R) \rangle \cdot \nabla F_{\beta}(R) + \frac{1}{2M} \langle \phi_{\alpha}(R), \nabla^2 \phi_{\beta}(R) \rangle F_{\beta}(R) \right) \quad (4)$$

The Born-Oppenheimer approximation consists of setting the right-hand side of Eq. (4) equal to zero (although the diagonal terms may fruitfully be retained).² The equations for the various F_{α} then decouple. We shall refer to this situation as the one-state Born-Oppenheimer approximation. Because of the largeness of the atomic to electronic mass ratio this is a good approximation unless the electronic wave functions ϕ_{α} exhibit an anomalously rapid variation as the internuclear separation is changed. We shall show that this is the case when two of the adiabatic curves with the same symmetry come very close to one another ("near crossing").

When there is a near crossing it is generally argued that the adiabatic states ϕ_{α} no longer provide a suitable basis for an expansion of the wavefunction. The problem is then reformulated either in a time dependent way³ using atomic wave functions or in a time independent way⁴ using simple

² L. D. Landau and E. M. Lifshitz, Quantum Mechanics (Pergamon Press, London-Paris, 1958) p. 275.

³ C. Zener, Proc. Roy. Soc. (London), A137, 696 (1932); L. Landau, Phys. Z. Sowjet Union, 2, 46 (1932); D. R. Bates, H. C. Johnston and I. Stewart, Proc. Phys. Soc. (London) 84, 517 (1964); C. A. Coulson and K. Zalewski, Proc. Roy. Soc. (London) A268, 437 (1962); D. R. Bates, Proc. Roy. Soc. (London) A257, 22 (1960).

⁴ N. F. Mott and H.S.W. Massey, The Theory of Atomic Collisions, Third Edition (Oxford University Press, London, 1965) Ch.p. 13.

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molecular orbitals.⁵ In both of these formulations the resulting potential curves cross and a set of coupled equations are considered which involve the two states that cross.

There are two disadvantages to this approach. Because of the crude wave functions used the electronic Hamiltonian will have large matrix elements connecting different states and it is therefore difficult to justify the use of only two electronic states in formulating the problem. In addition there is the esthetic disadvantage that the basis of the theory disappears if the wave functions are sufficiently improved so that the curves no longer cross.

In this paper we reformulate the problem starting from the adiabatic potential curves. The resulting equations for the nuclear wave functions are identical to those obtained in the conventional approach. However, all the parameters for the theory can be obtained from an inspection of the adiabatic curve. In addition, it is easy to justify the use of a two-state approximation when such an approximation is applicable.

II. THEORY

The general shape of the adiabatic energy curves for a near-crossing is illustrated by the solid curves labeled E_α and E_β in Fig. 1. The general feature of such potential curves is that the second derivative of the energy with respect to the internuclear separation (d^2E_α/dR^2) is large in the vicinity of the near crossing and that the curves asymptotically approach regions where the second derivative is much smaller. We shall show that in this transition region the adiabatic electronic wave functions $\phi_\alpha(R, \xi_{e1})$, and $\phi_\beta(R, \xi_{e1})$ are rapidly varying functions of the parameter R with the two

⁵ W. Lichten in IVth International Conference on the Physics of Electronic and Atomic Collisions (Science Bookcrafters Inc., Hastings on Hudson, 1965) p. 63; V. Fano and W. Lichten, *Phys. Rev. Letters* **14**, 627 (1965). The molecular orbital approach has the great advantage that it provides a large amount of qualitative information about the general nature of the potential curves at the cost of relatively little effort.

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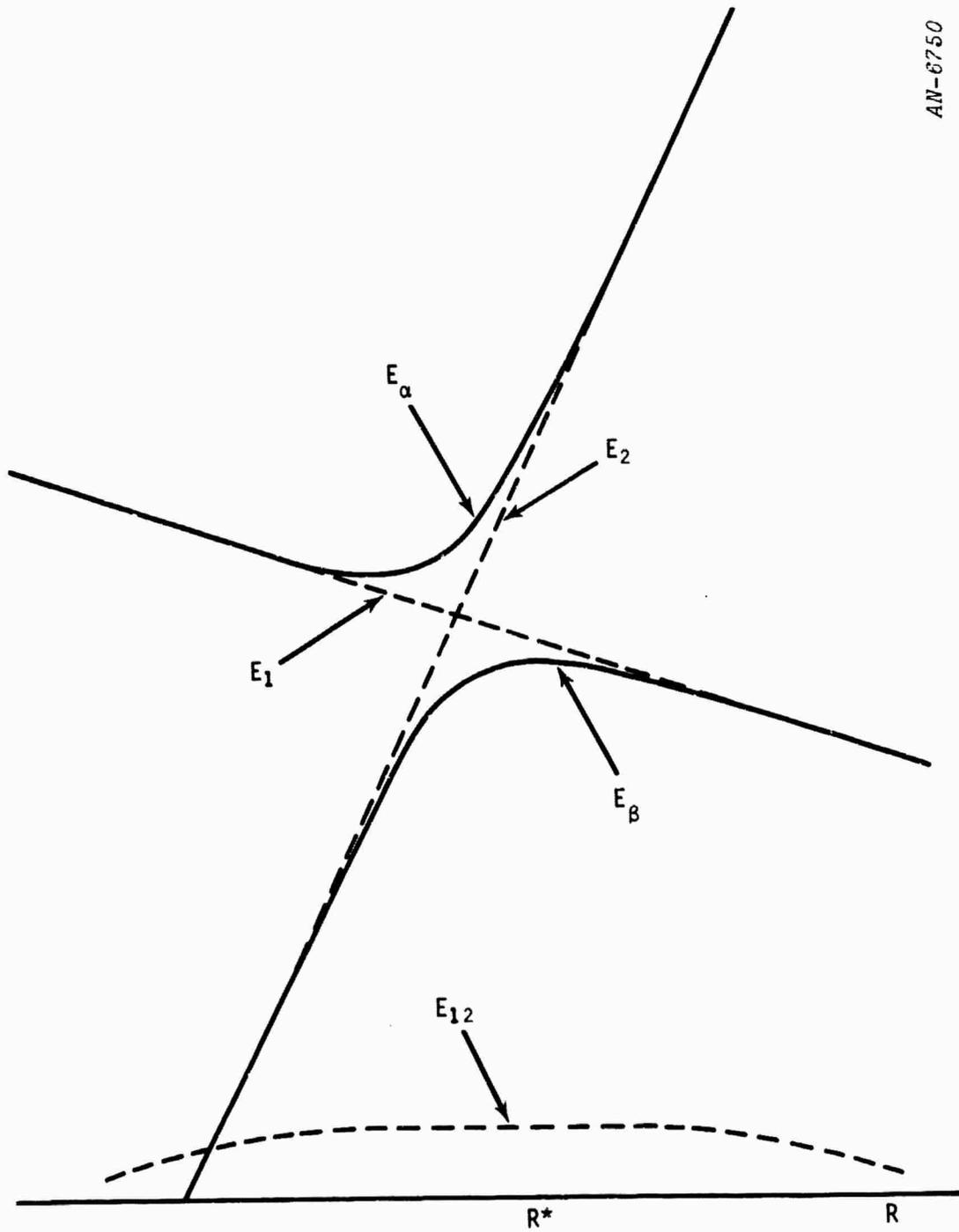


Figure 1. Potential Curves and Interaction Energy at a Near Crossing

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wave functions essentially changing roles as the transition region is crossed.

The difference of the slopes of the two energy curves changes sign as the transition region is crossed. The slopes must therefore be equal at some intermediate point R^* given by

$$\frac{\partial E_\alpha}{\partial R} = \frac{\partial E_\beta}{\partial R} = \lambda \text{ at } R = R^* . \quad (5)$$

In the transition region the electronic wave function $\phi_\alpha(R, \xi_{el})$ can be approximately represented as a linear combination of the wave functions $\phi_\alpha(R^*, \xi_{el})$ and $\phi_\beta(R^*, \xi_{el})$ so that⁶

$$\phi_\alpha(R) \approx A\phi_\alpha(R^*) + B\phi_\beta(R^*) . \quad (6)$$

The secular equations have the form

$$(E_\alpha(R^*) + \lambda\rho - E_\alpha(R)) A + \mu B \approx 0$$

$$\text{and } \mu A + (E_\beta(R^*) + \lambda\rho - E_\alpha(R)) B \approx 0 \quad (7)$$

$$\text{where } \rho = R - R^*$$

$$\text{and } \mu = \langle \phi_\alpha(R^*) | \hat{R} \cdot \frac{\partial H}{\partial R} | \phi_\beta(R^*) \rangle . \quad (8)$$

It is a trivial matter to solve these equations and we find

$$E_\alpha(R) \approx \bar{E} + \lambda\rho + \left(\frac{(\Delta E)^2}{4} + \mu^2 \rho^2 \right)^{1/2}$$
$$E_\beta(R) \approx \bar{E} + \lambda\rho - \left(\frac{(\Delta E)^2}{4} + \mu^2 \rho^2 \right)^{1/2} \quad (9)$$

⁶ In the following we shall generally omit the electronic coordinates ξ .

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$$\begin{aligned}\phi_{\alpha}(R) &\approx \sin \theta \phi_{\alpha}(R^*) + \cos \theta \phi_{\beta}(R^*) \\ \phi_{\beta}(R) &\approx -\cos \theta \phi_{\alpha}(R^*) + \sin \theta \phi_{\beta}(R^*)\end{aligned}\quad (10)$$

with

$$2\bar{E} = E_{\alpha}(R^*) + E_{\beta}(R^*), \quad \Delta E = E_{\alpha}(R^*) - E_{\beta}(R^*)$$

and

$$\cot \theta = -\frac{\mu\rho}{\frac{\Delta E}{2} + \left(\left(\frac{\Delta E}{2}\right)^2 + \mu^2\rho^2\right)^{1/2}}\quad (11)$$

The equations for $\phi_{\alpha}(R)$ and $\phi_{\beta}(R)$ are readily inverted to give

$$\begin{aligned}\phi_{\alpha}(R^*) &\approx \sin \theta \phi_{\alpha}(R) - \cos \theta \phi_{\beta}(R) \\ \phi_{\beta}(R^*) &\approx \cos \theta \phi_{\alpha}(R) + \sin \theta \phi_{\beta}(R)\end{aligned}\quad (12)$$

The linear combinations of $\phi_{\alpha}(R)$ and $\phi_{\beta}(R)$ occurring on the right-hand side of Eq. (12) are therefore slowly varying functions of R . The rapid changes in $\phi_{\alpha}(R)$ and $\phi_{\beta}(R)$ are compensated by the rapid variation of θ ($d\theta/dR = \mu/\Delta E$ at $R = R^*$). The particular linear combinations given by Eq. (12) are not the most convenient set since they do not asymptotically approach the adiabatic states. The sum and the difference of the right-hand sides of Eq. (12) provide more suitable combinations. We therefore define

$$\begin{aligned}\phi_1(R) &\equiv \cos \chi \phi_{\alpha}(R) + \sin \chi \phi_{\beta}(R) \\ \phi_2(R) &\equiv -\sin \chi \phi_{\alpha}(R) + \cos \chi \phi_{\beta}(R)\end{aligned}\quad (13)$$

where $\chi = \theta - 45^\circ$. To the left of the transition region $\chi \rightarrow 0$ so that $\phi_{\alpha} \rightarrow \phi_1$ and $\phi_{\beta} \rightarrow \phi_2$. At $R = R^*$, $\chi = 45^\circ$. To the right of the transition region $\chi \rightarrow 90^\circ$ so that $\phi_{\beta} \rightarrow \phi_1$ and $\phi_{\alpha} \rightarrow -\phi_2$. Since ϕ_1 and ϕ_2 do not change

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appreciably the functions ϕ_α and ϕ_β have suffered large changes and have essentially interchanged. The functions $\phi_1(R)$ and $\phi_2(R)$ provide a suitable basis to be used when making the Born-Oppenheimer approximation.⁷ The wave functions ϕ_1 and ϕ_2 can be used to define new potential curves indicated by the dotted line in Fig. 1. The diagonal elements of H_{e1} determine E_1 and E_2 and the off diagonal element determines E_{12} the interaction between the two curves E . We find

$$\begin{aligned} E_1(R) &= \cos^2 \chi E_\alpha(R) + \sin^2 \chi E_\beta(R) \\ E_2(R) &= \sin^2 \chi E_\alpha(R) + \cos^2 \chi E_\beta(R) \\ E_{12}(R) &= + \cos \chi \sin \chi (E_\beta(R) - E_\alpha(R)) \end{aligned} \quad (14)$$

We can now make the Born-Oppenheimer approximation with confidence and we get the coupled equations for the nuclear wave functions

$$\begin{aligned} \left(-\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\ell(\ell+1)}{2MR^2} + E_1(R) \right) F_1(R) + E_{12}(R) F_2(R) &= EF_1(R) \\ \left(-\frac{1}{2MR^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\ell(\ell+1)}{2MR^2} + E_2(R) \right) F_2(R) + E_{12}(R) F_1(R) &= EF_2(R) \end{aligned} \quad (15)$$

These are the usual equations for the two-state problem, except that in our case the potentials are determined from the adiabatic curves. The usual treatments of the two-state problem are therefore applicable.

All of the parameters needed to determine the nuclear wave functions can be obtained directly from the adiabatic potential curves except for

⁷ The electronic wave functions vary rapidly with internuclear separation in another circumstance - when there is an electronic resonance. The Born-Oppenheimer approximation can then not be directly applied and the appropriate treatment is quite analogous to ours with the resonant state playing a role similar to ϕ_1 and ϕ_2 . See T.F. O'Malley, Phys. Rev. 150, 14 (1966).

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the parameter which is defined by the matrix element in Eq. (8). However, if the near curve crossing is sufficiently close so as to invalidate the use of the one state Born-Oppenheimer approximation, μ can be obtained to sufficient accuracy by fitting the energy curves in the transition region with the hyperbola

$$(E_{\alpha}(R) - E_{\beta}(R))^2 - (E_{\alpha}(R^*) - E_{\beta}(R^*))^2 = 4\mu^2 (R - R^*)^2 . \quad (16)$$

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TREATMENT OF ANGULAR MOMENTUM IN MOMENTUM SPACE*

by

Peter J. Redmond

ABSTRACT

Equations are derived, in a momentum space representation, for the wave function of a many body system with a definite angular momentum. Invariance of the Hamiltonian under time reversal, parity, and exchange has simple consequences for a three-body system.

INTRODUCTION

The general form of the wave function of a system having a definite angular momentum has been given by Wigner. He showed that the dependence of the wave function on the orientation could be indicated explicitly so that the dynamical problem involved a set of functions f_K which depend only on quantities which are invariant under rotations.

Although the general form of the wave function is known, considerable labor is necessary before equations relating the f_K 's can be obtained. All the treatments familiar to the author consider the problem in configuration space. The kinetic energy is then represented by differential operators and the central problem is to express these deviations in terms of derivatives with respect to angles and derivatives with respect to rotational invariants. It is in the nature of this process of changing variables that a successful completion of the program for a three-body system is of little assistance if one is confronted by a four-body problem.

It is often convenient to consider a problem in momentum space rather than configuration space (for example, in a scattering problem). It is the

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purpose of this paper to derive the equations describing a many body system with a definite angular momentum in the center of mass frame. We believe that the results are structurally much simpler than those obtained in configuration space. In particular, the equations have the same structure for a four-or-more-body problem as they do for a three-body problem.

The paper is divided into four sections. Section 1 is the introduction which you have almost finished reading. In Section 2 a thumbnail sketch of some aspects of the general theory of angular momentum is presented in order to establish a notation and a set of conventions. The third section is devoted to a derivation of our central result. In the last section the effects of parity, exchange, and time reversal invariance are discussed for a three-body system.

SOME ASPECTS OF THE GENERAL THEORY OF ANGULAR MOMENTUM

The effects of rotations may be described from two different points of view. According to the first point of view one considers the change in description of a fixed geometrical configuration produced by a rotation of the coordinate axes. According to the second point of view rotations are used to describe the motion of a geometrical configuration relative to a fixed set of coordinate axes. Throughout this paper we adopt the second point of view.

We consider functions $\psi(\{p\})$ of the set of vectors p_1, p_2, \dots, p_N ($= \{p\}$) which we denote by an inner product

$$\psi(\{p\}) = \langle \{p\} | \psi \rangle \quad (1)$$

An infinitesimal rotation about the \hat{n} axis through an angle $\delta\phi$ causes a change in the vector p_α by an amount δp_α given by

$$\delta p_\alpha = \delta\phi \hat{n} \times p_\alpha \quad (2)$$

This causes an infinitesimal change in the function $\psi(\{p\})$ which may be computed by taking the first term in a Taylor expansion

$$\delta \psi(\{p\}) = \sum_\alpha \delta\phi \hat{n} \times p_\alpha \cdot \frac{\partial}{\partial p_\alpha} \psi(\{p\}) \quad (3)$$

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This may be rewritten as

$$\delta \psi(\{p\}) = i\delta\phi \langle \{p\} | \hat{n} \cdot L | \psi \rangle \quad (4)$$

where we have used $\frac{\partial}{\partial p} = i\mathbf{r}$ and $L = \sum_{\alpha} \mathbf{r}_{\alpha} \times \mathbf{p}_{\alpha}$. This may be integrated to give

$$\psi(\{p\}R(\hat{n},\phi)) = \langle \{p\} | e^{i\phi\hat{n} \cdot L} | \psi \rangle \quad (5)$$

which describes the effect of a finite rotation, $R(\hat{n},\phi)$, through an angle ϕ about the axis \hat{n} . We have given this derivation to emphasize the fact that Eq. (5) is a symbolic operator characterization of a generalized Taylor expansion and does not depend on the nature of the function ψ (except that we assume the expansion converges).

If the rotation R corresponds to the rotation $R_1 (= R(\hat{n}_1, \theta_1))$ followed by the rotation $R_2 (= R(\hat{n}_2, \theta_2))$, then

$$\langle \{p\} | R | \psi \rangle = \langle \{p\} | e^{i\hat{n}_1 \cdot L\theta_1} e^{i\hat{n}_2 \cdot L\theta_2} | \psi \rangle \quad (6)$$

Since we wish to use the symbols R both in abstract arguments and as symbols for the operators $e^{i\hat{n} \cdot L\theta}$ we shall denote the product of two rotations in such a way that the symbols are ordered from left to right,

$$R = R_1 R_2 \quad (7)$$

We shall make frequent use of the identity

$$R_1^{-1} R(\hat{n}, \theta) R_1 = R(\hat{n}R_1, \theta) \quad (8)$$

which may be proven by simple geometric arguments or by manipulation of the operator expressions using the commutation relations

$$L \times L = iL \quad (9)$$

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We shall make frequent use of the irreducible representations of the rotation group defined by

$$D_{M',M}^L(R(\hat{n},\theta)) = \langle L,M' | e^{i\theta\hat{n}\cdot L} | L,M \rangle \quad (10)$$

Since any rotation can be expressed as a rotation about the z axis followed by a rotation about the y axis followed finally by another rotation about the z axis (Euler angle representation) it is only necessary to give a formula for

$$d_{M',M}^L(\beta) = \langle L,M' | e^{i\beta L_y} | L,M \rangle \quad (11)$$

If the usual phase conventions are adopted for the matrix elements of L , then Eq. (11) leads to the formula given by Wigner.

DERIVATION OF CENTRAL RESULT

For a three-body system interacting through two body central forces the time independent Schrödinger equation is

$$\begin{aligned} \left(E - \frac{p_1^2}{2M_1} - \frac{p_2^2}{2M_2} - \frac{p_3^2}{2M_3} \right) \langle p_1, p_2, p_3 | \psi \rangle \\ = \int dg V_{12}(q^2) \langle p_1 + q, p_2 - q, p_3 | \psi \rangle + \dots \end{aligned} \quad (12)$$

where the omitted terms involve V_{13} and V_{23} . The total linear momentum is a constant of the motion and we shall work in the frame where this vanishes. The three momenta then form a triangle and the wave function depends on the magnitude of the momenta and on the orientation of the triangle.

We specify the orientation of the triangle by indicating the rotation R_ρ which carries the momentum triangle from some specified reference orientation ρ to its actual position. We shall introduce three standard reference orientations labeled by $\rho = 1, 2, 3$. These are defined by requiring that the

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three momenta lie in the X-Y plane and that the directed normal is in the z direction. For $\rho = j = 1, 2, 3$ the momentum p_j is in the y direction. These standard reference orientations are illustrated in Fig. 1. The wave function at the point $\{p\}$ is related to its value at the reference position $\{\rho\}$ by the operator equation

$$\langle \{p\} | \psi \rangle = \langle \{\rho\} | R_\rho | \psi \rangle \quad (13)$$

The potential energy terms change both the magnitude of the particle momenta and the orientation of the momentum triangle. These effects are illustrated in Fig. 2 for the term V_{12} . The momentum triangle rotates about the p_3 axis by the angle ϕ and the magnitude of the momentum p_1 and p_2 is changed to p_1' and p_2' .

Let R_ρ' be the rotation which takes the momentum triangle $p_1' p_2' p_3$ from its reference position ρ to its final position. It is necessary to find a relationship between R_ρ' and R_ρ . The rotation R_ρ' can be performed in three steps. First rotate the triangle $p_1' p_2' p_3$ from its reference position ρ to the position given in Fig. 1(c). We denote this rotation by $R_{\rho,3}'$. This is then followed by the rotation R_3 which takes p_3 into its final position and the plane of the momentum triangle into the $p_1 p_2 p_3$ plane. This is then followed by a rotation through an angle ϕ about the p_3 axis. Thus

$$R_\rho' = R_{\rho,3}' R_3 R(\hat{p}_3, \phi) \quad (14)$$

By using Eq. (8) this can be rewritten

$$R_\rho' = R_{\rho,3}' R(\hat{y}, \phi) R_3 \quad (15)$$

Similar reasoning leads to an expression for R_ρ ,

$$R_\rho = R_{\rho,3} R_3 \quad (16)$$

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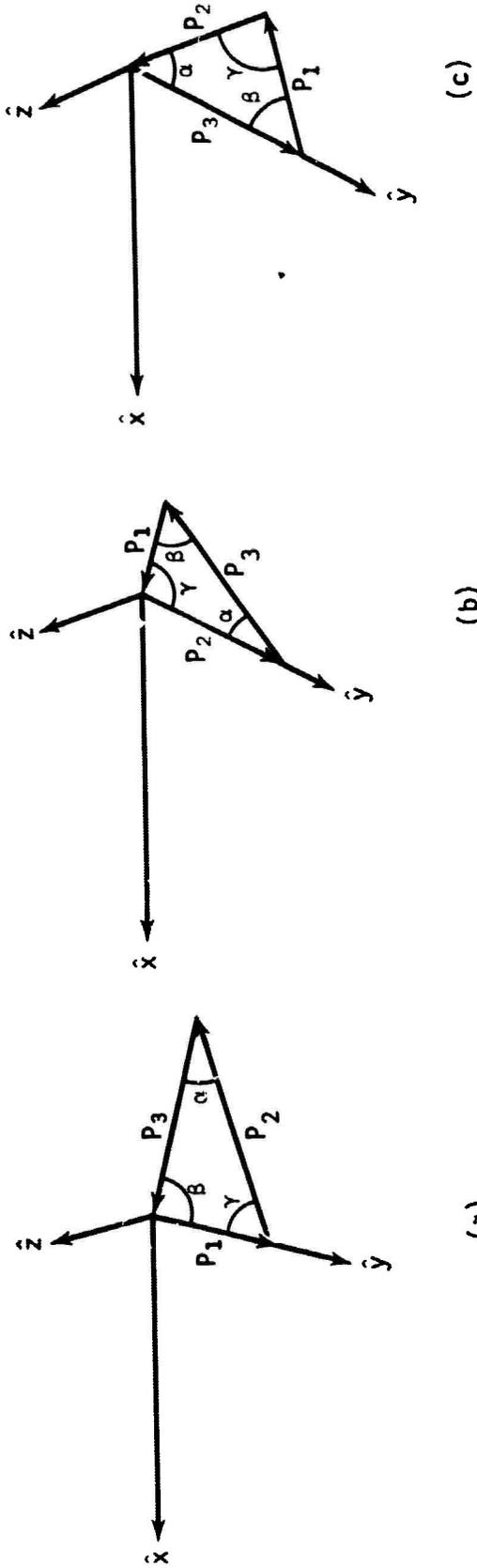


Figure 1. The Three Standard Reference Orientations

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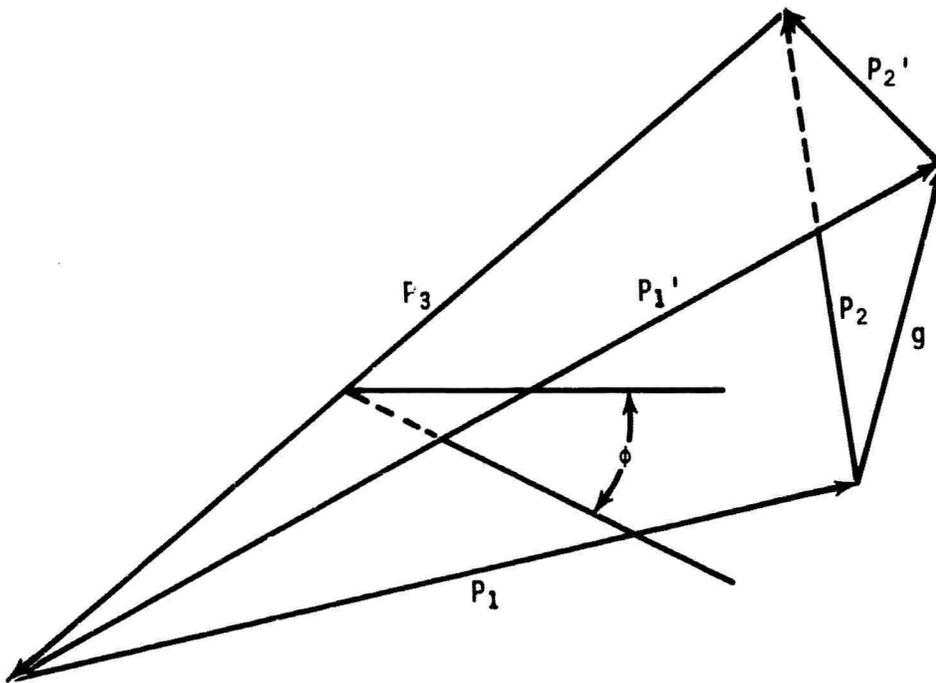


Figure 2. Effect of a Momentum Transfer

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By eliminating R_3 we obtain

$$R_\rho' = R_{\rho,3}' R(\hat{y}, \phi) R_{3,\rho} R_\rho \quad (17)$$

where $R_{3,\rho} = R_{\rho,3}^{-1}$.

It is also necessary to change variable from q to p_1' , p_2' , and ϕ . The Jacobian of this transformation is most easily found in two steps. We introduce the symbol Δ for the area of the triangle, so that

$$16\Delta^2 = (p_1+p_2+p_3)(-p_1+p_2+p_3)(p_1-p_2+p_3)(p_1+p_2-p_3) \quad (18)$$

Then $2\Delta'/p_3$, $p_3 \cdot p_1'/p_3$, and ϕ form a set of cylindrical coordinates. Thus

$$dq = (4/p_3^3) \Delta' d\Delta' d(p_1' \cdot p_3) d\phi \quad (19)$$

It is then relatively easy to make the additional transformation to obtain

$$dq = (1/|p_1+p_2|) p_1' p_2' dp_1' dp_2' d\phi \quad (20)$$

An expression for q^2 is also required. After a little algebra one finds

$$\begin{aligned} q^2 &= (1/p_3^2) \left[(q \times p_3)^2 + (q \cdot p_3)^2 \right] \\ &= \left[(4/p_1+p_2)^2 \right] \left[(\Delta^2 + \Delta'^2 - 2\Delta\Delta' \cos \phi) + (1/16)(p_1^2 + p_2^2 - p_1'^2 - p_2'^2)^2 \right] \end{aligned} \quad (21)$$

Substituting this into Eq. (12) we obtain

$$\begin{aligned} &\left(E - \frac{p_1^2}{2M_1} - \frac{p_2^2}{2M_2} - \frac{p_3^2}{2M_3} \right) \langle \{p\}_\rho | R_\rho | \psi \rangle = \\ &\left(\frac{1}{|p_1+p_2|} \right) \int p_1' dp_1' p_2' dp_2' d\phi v_{12}(q^2) \langle \{p'\}_\rho | R_{\rho,3}' R(\hat{y}, \phi) R_{3,\rho} R_\rho | \psi \rangle + \dots \end{aligned} \quad (22)$$

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We have not yet used the fact that ψ is an eigenstate of the angular momentum operators L^2 and L_z . If ψ is an eigenfunction of L^2 and L_z with eigenvalues $L(L+1)$ and M it is possible to express the matrix elements of the rotation operators in terms of the functions D^L .

The functions f defined by

$$\delta(\Sigma p) f_{L,M}^{\rho}(p_1, p_2, p_3) \equiv \langle \{p\}_{\rho} | \psi_{L,M} \rangle \quad (23)$$

depend only on the invariants $|p_1|$, $|p_2|$ and $|p_3|$. They then satisfy the equation

$$\left(E - \frac{p_1^2}{2M_1} - \frac{p_2^2}{2M_2} - \frac{p_3^2}{2M_3} \right) f_{L,K}^{\rho}(p_1, p_2, p_3) = \Sigma_K (1/|p_1+p_2|) \times \int p_1' p_2' dp_1' dp_2' d\phi v_{12}(q^2) D_{K',K}^L(R_{\rho,3} R(\hat{y}, \phi) R_{3,\rho}) \times f_{L,K'}^{\rho}(p_1', p_2', p_3) + \dots \quad (24)$$

The relationship between the wave function at an arbitrary point $\{p\}$ and the f 's is given by

$$\langle \{p\} | \psi_{L,M} \rangle = \langle \{p\}_{\rho} | R_{\rho} | \psi_{L,M} \rangle = \delta(\Sigma p) \Sigma_K f_{L,K}^{\rho}(p_1, p_2, p_3) D_{K,M}^L(R_{\rho}). \quad (25)$$

It is a simple exercise, which we leave to the reader, to demonstrate that Eqs. (24) and (25) imply that the wave function $\langle \{p\} | \psi \rangle$ is independent of what choice is made for the reference orientation ρ although the functions f^{ρ} do, of course, depend on this choice.

If the reference orientation ρ is such that the momentum triangle is in the x - y plane then $R_{\rho,j}$ is a rotation about the z axis so that D occurring in Eq. (24) is a simple phase factor times d defined in Eq. (11)--that is, we have the usual Euler angle representation of the rotation group. In particular $R_{1,2} = R(\hat{z}, \pi+\gamma)$, $R_{2,3} = R(\hat{z}, \pi+\alpha)$, and $R_{3,1} = R(\hat{z}, \pi+\beta)$.

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It should be noted that Eqs. (22), (23) and (24) are true for any number of particles if we add the needed additional kinetic energy terms on the left-hand sides and provide the additional scalar arguments for the functions f . There are however two fairly serious geometrical complications. The variables p_1, p_2, \dots, p_N are no longer a complete set of scalars and an additional $3N-9$ scalars must be introduced. Some of these additional scalars will change due to the action of V_{12} and will be complicated functions of p_1', p_2', ϕ and the initial set of scalars. In addition the determination of the rotations $R_{\rho, j}$ will involve rather difficult geometrical considerations.

EFFECTS OF PARITY, EXCHANGE, AND TIME REVERSAL INVARIANCE

For a three-body system it is fairly easy to determine the effects of a parity or an exchange transformation of the functions f .

For a three-body system the parity transformation is equivalent to a rotation through 180° about the normal, \hat{n} , to the momentum triangle. This is equivalent to first rotating the reference state by 180° about the z axis provided the reference state lies in the x - y plane. For even (odd) parity states we obtain

$$\begin{aligned} \pm \langle \{p\} | \psi \rangle &= \pm \langle \{p\}_\rho | R_\rho | \psi \rangle \\ &= \langle \{-p\} | \psi \rangle = \langle \{p\}_\rho | R(\hat{z}, \pi) R_\rho | \psi \rangle \end{aligned} \quad (26)$$

This immediately leads to the relation

$$\begin{aligned} &(\text{PARITY}) \\ \pm f_{L,K}^\rho &= (-1)^K f_{L,K}^\rho \end{aligned} \quad (27)$$

If particles 1 and 2 are indistinguishable it is desirable to know the effect on the f 's of their exchange. For this purpose it is convenient to use the reference orientation illustrated in Fig. 1(c) where p_3 is along the y axis. The effect of an exchange is illustrated in Fig. 3 and it is seen that the directed normal to the plane points in the $-z$ direction

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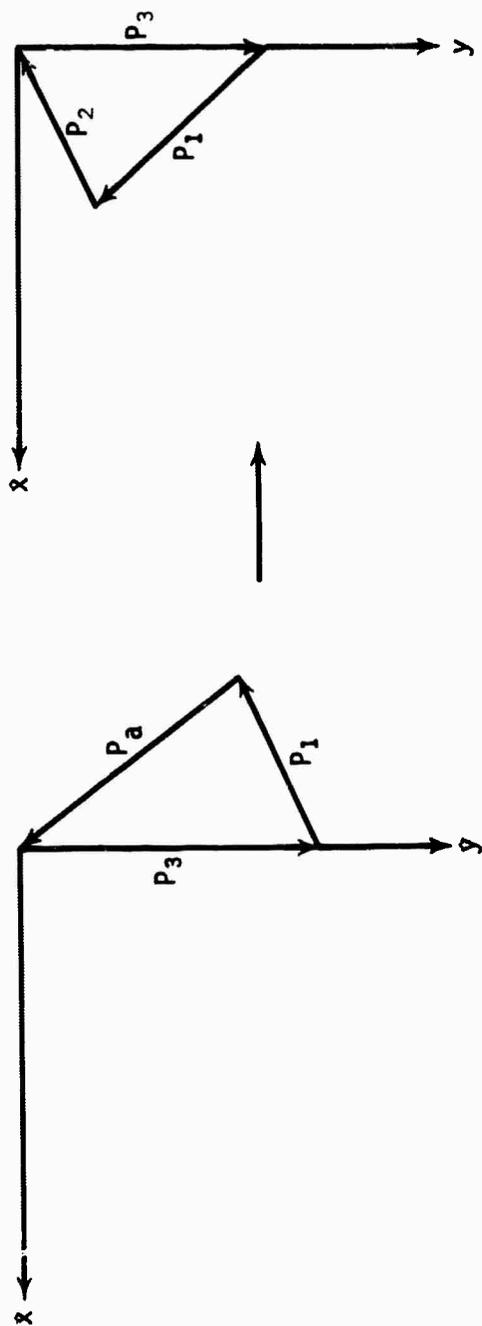


Figure 3. Effect of Exchange of Particles One and Two

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instead of the z direction. This can be modified by performing a rotation about the y axis of 180° . For states even (+) or odd (-) under exchange we find

$$f_{L,K}^3(p_1, p_2, p_3) = \sum_{K'} f_{L,K'}^3(p_2, p_1, p_3) \langle LK' | R(\hat{y}, \pi) | LK \rangle \quad (28)$$

Using

$$D_{K',K}^L(R(\hat{y}, \pi)) = \delta_{K',-K} (-1)^{L-K} \quad (29)$$

we find

$$f_{L,K}^3(p_1, p_2, p_3) = (-1)^{L-K} f_{L,-K}^3(p_2, p_1, p_3) \quad (30)$$

If all three particles are equivalent it is possible to use equations analogous to Eq. (30) for the exchange of any pair. These results combined with

$$f_{L,K}^j = \sum_{K'} f_{L,K'}^k D_{K',K}^L(R_{k,j})$$

provides all the needed information -- unfortunately in a rather cumbersome form. Attempts by the author to define a reference orientation which treats all three particles symmetrically, and which leads to simpler expressions for the effects of exchange, have been unsuccessful.

The final symmetry transformation we consider is the behavior under time reversal. Following Wigner we note that solutions can be chosen such that

$$\langle \{-p\} | \psi_{L,M} \rangle^* = (-1)^M \langle \{p\} | \psi_{L,-M} \rangle \quad (31)$$

If we apply E. (26) and observe that

$$D_{K,M}^L(R)^* = (-1)^{M-K} D_{-K,-M}^L(R) \quad (32)$$

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we immediately obtain

TIME REVERSAL

$$(f_K^\rho)^* = f_{-K}^\rho \quad (33)$$

Since we have used Eq. (26), the reference orientation ρ must be such that the momentum triangle lies in the x-y plane. For bound state problems the overall phase of the wave function can always be chosen so that Eq. (33) is satisfied. For scattering problems it is also necessary that the inhomogeneous terms be chosen so as to satisfy Eq. (33). (This may always be done.)

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ON THE SLOPE OF ENERGY CURVES AS THEY ENTER THE CONTINUUM *

by

Peter J. Redmond

ABSTRACT

Let the Hamiltonian $H(\lambda)$ have a bound state with binding energy $E(\lambda)$ such that the $E(\lambda) \rightarrow 0$ as $\lambda \rightarrow \lambda^*$. It is shown that $dE(\lambda)/d\lambda = 0$ at $\lambda = \lambda^*$ for s-states and that $dE(\lambda)/d\lambda \neq 0$ for higher angular momentum. As an application of this theorem it is shown that there is a low lying p-wave resonance in the scattering of an electron by molecular hydrogen.

According to the best available calculation¹ the lowest lying adiabatic potential curve for the system $H + H^-$ intersects the ground state H_2 potential at a point to the right of the H_2 minimum. It has been suggested² that the two curves should be tangential at the point of intersection whereas the numerical calculations indicate that this is not so. Which of these two possibilities is realized is important in deciding whether it is reasonable to consider extending the $H + H^-$ curve beyond the intersection point and interpreting it as a potential resonance. The same question arises for any $A + B^-$ system and in many other molecular problems.

We shall show that the essential features of the problem are present in a very much simpler situation. We consider the motion of a particle governed by a Hamiltonian containing a potential which depends on a parameter λ . It is assumed that the Hamiltonian has a bound state with energy $E(\lambda)$ over some range of values for λ and that $E(\lambda) \rightarrow 0$ as $\lambda \rightarrow \lambda^*$. We

* Submitted to Phys. Rev.

¹ H. S. Taylor and F. E. Harris, J. Chem. Phys. 39, 1012, 1963.

² Private communication, B. F. Gray.

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shall show that $dE(\lambda)/d\lambda = 0$ at $\lambda = \lambda^*$ for s states and that, in general, $d(E(\lambda))/d\lambda \neq 0$ for higher angular momentum.

Consider the Schrodinger equation ($\kappa = 1$)

$$\left[-\frac{1}{2mr} \left(\frac{d}{dr} \right)^2 r + \frac{\ell(\ell+1)}{2mr^2} + V(r, \lambda) \right] \phi(r, \lambda) = E(\lambda) \phi(r, \lambda) . \quad (1)$$

For simplicity we assume that $V(r, \lambda) = 0$ for $r > r_0$ although this is not essential to the argument. The slope of the energy curve is given by

$$\frac{dE(\lambda)}{d\lambda} = \int_0^{r_0} \phi^2(r, \lambda) \frac{\partial}{\partial \lambda} V(r, \lambda) r^2 dr . \quad (2)$$

We now consider the behavior of the s-wave solutions as $E(\lambda) \rightarrow 0$.

At distances greater than r_0 the wave function is proportional to $e^{-\kappa r}/r$ where κ is defined by $E(\lambda) = -\kappa^2/2m$. Let the solution to Eq. (1) for $r < r_0$ be denoted by $\chi(r, \lambda)$ where we normalize $\chi(r, \lambda)$ to unity,

$$\int_0^{r_0} \chi^2(r, \lambda) r^2 dr = 1 . \quad (3)$$

Then the wave function $\chi(r, \lambda)$ will approach a definite well defined limit as $E(\lambda) \rightarrow 0$. (As a simple example: for a square well potential of range r_0 and variable depth $\chi(r, \lambda) \rightarrow (2/r_0)^{1/2} \sin(\pi r/2r_0)/r$.) The normalized wave function then is given by

$$\begin{aligned} \phi(r, \lambda) &= N \chi(r, \lambda) , \quad r < r_0 \\ &= N(r_0/r) \chi(r_0, \lambda) e^{-\kappa(r-r_0)} , \quad r > r_0 . \end{aligned} \quad (4)$$

The normalization factor is readily obtained

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$$N^2 = (1 + r_0^2 \chi^2(r_0, \lambda) / 2\kappa)^{-1} \quad (5)$$

and

$$N^2 \rightarrow 2\kappa / \chi^2(r_0, \lambda) r_0^2 \rightarrow 0 \quad \text{as } E(\lambda) \rightarrow 0 .$$

The possibility that the conclusion $N^2 \rightarrow 0$ could be incorrect because $\chi(r_0, \lambda) \rightarrow 0$ can be ruled out by noting that the logarithmic derivative of the r times the wave function must be continuous at $r = r_0$. This gives

$$\frac{1}{r_0 \chi(r_0, \lambda)} \frac{d}{dr} r \chi(r, \lambda) \Big|_{r=r_0} = -2\kappa \rightarrow 0 . \quad (6)$$

so that $dr\chi/dr \rightarrow 0$ at $r = r_0$. If $\chi(r_0, \lambda)$ also approached zero then $\phi(r, \lambda)/N$ would approach a function which was identically zero everywhere. This contradicts the assumption that a bound state exists in the vicinity of $E = 0$.

In order to illustrate the argument for higher angular momentum we consider a p-state. The wave function is then given by

$$\begin{aligned} \phi(r, \lambda) &= N \chi(r, \lambda) , \quad r < r_0 \\ &= N(r_0/r) \chi(r_0, \lambda) e^{-\kappa(r-r_0)} (1 + 1/\kappa r) / (1 + 1/\kappa r_0) , \quad r > r_0 . \end{aligned} \quad (7)$$

An expression for the normalization factor is easily written and one readily finds that as $E(\lambda) \rightarrow 0$ $N^2 \rightarrow (1 + r_0^3 \chi^2(r_0, \lambda^*))^{-1}$. The argument is readily extended to higher angular momentum and

$$N_\ell^2 \rightarrow \left(1 + r_0^3 \chi^2(r_0, \lambda^*) / (2\ell - 1)\right)^{-1} , \quad \ell \geq 1 . \quad (8)$$

Since the normalization factor approaches a finite non-zero value the slope $dE/d\lambda$ given by Eq. (2) will generally be non-zero.

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The above simple treatment of a simple model can be described in more general terms which indicate the wide applicability of the results. Consider a many body Hamiltonian which depends on a varying parameter such that the binding energy of the system approaches zero. As this limit is approached one of the particles will tend to separate from the remaining particles. At points where the separation distance, r , between these two components is very large the wave function is a product of a bound state function of the particles left behind multiplied by $Y_\ell^m(\theta, \phi)/r^{\ell+1}$,³ where ℓ is the relative angular momentum of the two components. For $\ell = 0$ the asymptotic wave function is not normalizable at zero binding energy so that the probability that the separated particle is in the range of the forces of the bound state left behind goes to zero. For higher angular momentum the asymptotic wave function is normalized so that the separated particle continues to interact with the remaining particles.

The result is a manifestation of the angular momentum potential barrier. The non-vanishing of $dE/d\lambda$ for $\ell \neq 0$ suggests that the energy curve may be extrapolated into the continuum where it would be identified as a resonance.

As an illustration of these ideas we consider the lowest potential curves of the H_2 molecule and HH^- system.⁴ The general shape of these curves is illustrated in Fig. 1 and the question to be decided is whether or not the curves are tangential at the point of intersection. It is easily seen that the arguments presented above apply to the difference in energy between the two curves. The H_2^- curve can be loosely described as being made up of the molecular orbitals $(\sigma_g)^2 \sigma_u$. At the point of intersection the extra electron (σ_u) in the HH^- system is in a p-state relative

³ There are also terms with lower inverse powers of r but these are multiplied by powers of K such that the products do not contribute to the normalization integral.

⁴ In application it is important that the long range force experienced by the odd particle is dominated by the centrifugal barrier. This is satisfied for the $e^- - H_2$ system.

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to the H_2 molecule so that the curves cross obliquely. This suggests that there should be a low lying p-state resonance in the scattering of electrons by H_2 .⁵

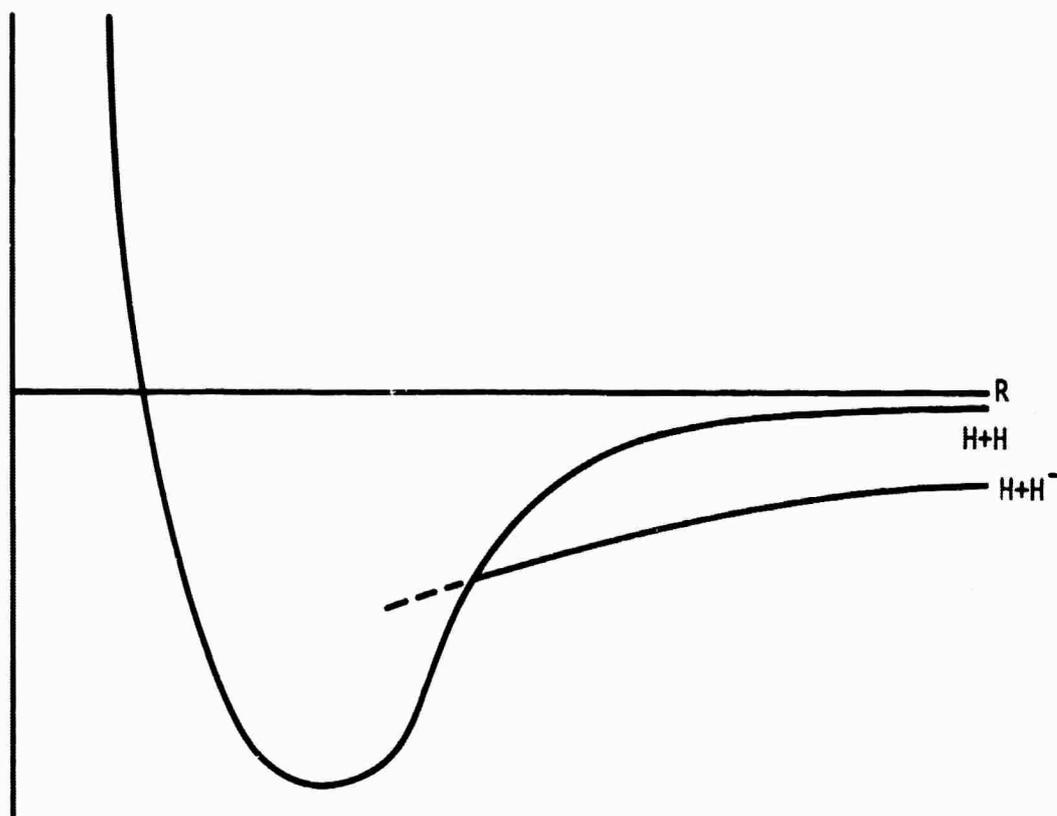


Figure 1. Lowest Lying Potential Curves of H_2 and HH^-

⁵ Experimental evidence for such a resonance, as well as references to previous theoretical and experimental studies, is contained in G. J. Schulz and R. K. Asundi, Phys. Rev. Letters 15, 946, (1965).

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13. ABSTRACT			
The following papers are presented in this report:			
1. Operator for Time Delay Induced by Scattering			
2. A Note on Scattering Variational Principles			
3. Integral Equations for Multi-Channel Collisions			
4. Calculation of Dissociative Attachment in Hot O ₂			
5. Quasi-Adiabatic Molecular States: An Alternative to the Non-Crossing Rule			
6. Theory of Resonant Dissociative Recombination			
7. Formulation of the Two State Problem in Terms of Adiabatic Potential Curves			
8. Treatment of Angular Momentum in Momentum Space			
9. On the Slope of Energy Curves as They Enter the Continuum			

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
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	Electron Distribution						
	Electronic Wave Function						
	Electron Density						
	Hot O ₂						
	Non-Crossing Rule						
	Nuclear Energy						
	Multi-Channel Collision						
	Quantum-Mechanics						
	Resonance						
	Recombination						
	Scattering						
	Vibrational Levels						