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Theory of Atomic Collisions with Negative Ions: Associative Detachment*†

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In this paper we consider the problem of atomic collisions with negative ions and give special attention to the rearrangement process of associative electron detachment. After the various possible processes, the interaction potentials, and the related problems of potential curves are described physically, a theoretical formulation of the problem is presented, ranging from general formalism to explicit formulas for the reaction cross section and the rate coefficient. In the general formalism, transition matrices are derived for direct and resonance reactions as well as for potential and resonance scatterings. The process of associative detachment is then treated explicitly, using these derived expressions. It is shown that because of the configuration interaction of the electronic motion with continua, the nuclear motion is taking place in a complex potential. The propagation of a nuclear state in such a complex potential is treated in some detail. Various implications of the derived theoretical results are discussed in connection with experimental observations.

I. INTRODUCTION

THE problem of atomic collisions with negative ions is of interest both from the standpoint of basic theory and from the standpoint of practical application. Since in general negative ions[1] have at the most a few bound states, and since the corresponding electron affinities are usually small, one therefore expects that electrons may easily be detached from the ions upon collisions with other atoms or molecules at energies greater than the electron affinities.[2,3] The measured rate coefficients indicate recently that, at energies lower than the corresponding electron affinities, the detachment rates are also large and for some cases they may even be larger than those measured at higher energies.[4] It is therefore interesting to investigate the detailed detachment mechanism at such low energies. From the energy considerations, it is obvious that electron detachment at such low energies may take place by the formation of stable neutral molecules; this is known as associative detachment. If the rate coefficients for such processes are indeed very large, the possibility that free oxygen atoms in the ionosphere may release electrons which are bound to negative ions would become significant. This then makes the associative-detachment process also of great practical interest.

Although negative ions in general do not have many bound states, they usually have a great number of auto-ionization states with a variety of widths.[5] Such auto-ionization states play an essential role in yielding the large detachment rate at low energies, since when atom A and ion B^- slowly come close to each other, their electronic states may gradually merge into auto-ionization states of the ion AB^-. These auto-ionization states may then decay into some states of AB lying below via auto-ionization, thus stabilizing the process of associative detachment. Clearly, this process depends strongly on the magnitude of the auto-ionization width.

Experimental studies of associative detachment[3] usually involve the measurement of rate coefficients which, though of great importance to the kinetics of the problem, yields little information concerning the detailed mechanism of the process. Detailed cross-section measurements for the reverse process, dissociative attachment, have been carried out for a number of gases.[6–9] Relevant information can then be deduced from these measurements with the help of the available theories for dissociative attachment.[10–12] There exist, however, uncertainties concerning the statistical factors in the information deduced. It is therefore desirable to study the

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† Parts of this work were presented as an invited paper at the Symposium on Physics and Chemistry of the Lower Atmosphere sponsored by the Defense Atomic Support Agency, Boulder, Colorado, June, 1966.

[1] L. M. Branscomb, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 4; B. L. Moiseiwitsch, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates (Academic Press Inc., New York, 1965), p. 61.

[2] Yu. N. Demkov, Zh. Eksperim. i Teor. Fiz. **46**, 1126 (1964). [English transl.: Soviet Phys.—JETP **19**, 762 (1964)].

[3] J. L. Pack and A. V. Phelps, J. Chem. Phys. **44**, 1870 (1966); **45**, 4316 (1966).

[4] A. V. Phelps and E. E. Ferguson (private communications).

[5] See for example, the review article by P. G. Burke, Advan. Phys. **14**, 521 (1965).

[6] V. I. Khvostenko and V. M. Dukel'sky, Zh. Eksperim. i Teor. Fiz., **33**, 851 (1957) [English transl.: Soviet Phys.—JETP **6**, 657 (1958)]; M. A. Biondi and R. E. Fox, Phys. Rev. **109**, 2012 (1958); G. J. Schulz, *ibid.* **113**, 816 (1959).

[7] T. E. Sharp and D. D. Briglia, Phys. Rev. Letters **14**, 544 (1965); D. Rapp and D. D. Briglia, J. Chem. Phys. **43**, 1480 (1965).

[8] G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965).

[9] R. N. Compton, G. S. Hurst, L. G. Chintophoron, and P. W. Reinhardt, Oak Ridge National Laboratory Report, ORNL-TM-1409, 1966 (unpublished).

[10] (a) J. C. Y. Chen, Phys. Rev. **148**, 66 (1966); (b) **129**, 202 (1963).

[11] J. N. Bardsley, A. Herzenberg, and F. Mandl, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 415.

[12] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

problem directly. The present paper presents such a theoretical investigation of the problem.

The plan of the paper is as follows. In Sec. II, a general discussion of various physical aspects of atomic collisions with negative ions is given. Attention is drawn to some ambiguities in interpreting potential curves for auto-ionization states of the negative molecular ions. An alternative model which removes these ambiguities is proposed for the process of dissociative attachment of electrons by hydrogen molecules near the threshold. In Sec. III, a general theoretical treatment of the problem of atomic collision with negative ions is presented. In this treatment, we have utilized projection-operator techniques. (The appropriate projection operators are derived in Sec. V.) Transition matrices are derived for multichannel direct and resonance reactions, as well as for potential and resonance scatterings. The processes of associative detachment and electron transfer are then treated explicitly in Sec. IV as both direct and resonance reactions. Various implications of the derived theoretical results are discussed in connection with experimental observations. Finally in Sec. V, the explicit projection operators are constructed for the system of interest.

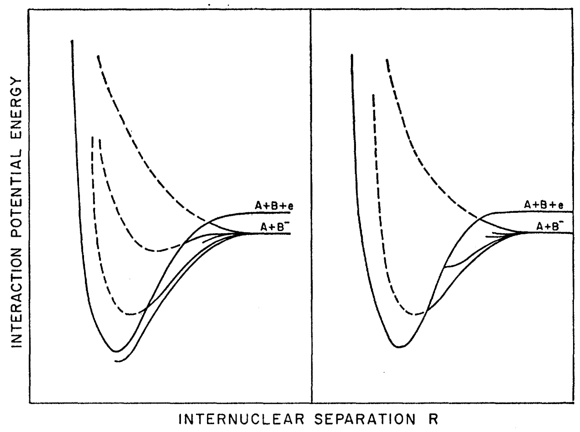

FIG. 1. Illustration of the potential curve for molecule AB with a continuum electron and of the interaction potential between atom A and negative ion B^-. The dashed curves represent the real parts of the interaction potential.

II. GENERAL DISCUSSION

Let us consider a system in which an atom A slowly approaches a negative ion B^- in their ground states. Their averaged trajectory is dictated by an interaction potential lying asymptotically below the corresponding asymptotic potential of AB (see Fig. 1). As they approach each other, their electronic states gradually merge into that of the negative molecular ion AB^-. The strong local electric field created along the internuclear axis will then remove the degeneracy and cause the interaction potential to split according to the net resultant momentum along the internuclear axis. Several typical situations may arise dependeing on the initial angular momenta and the spin symmetries of A and B^-,[13] and on the electron affinity of the molecule AB.

When the molecule AB has an electron affinity in its ground state [Fig. 1(a)], there will always be a possibility that the system will merge into the ground electronic state of AB^- and that the nuclei will then oscillate in the field provided by this state. Unless the system AB^- is stabilized by a third body (or by radiation), it will dissociate adiabatically so that the atom A and ion B^- will move apart in the time-reversed sense. Associative detachment,

$$A+B^- \rightarrow AB+e, \tag{2.1}$$

may occur in this case only when the colliding energy coincides with a nuclear-energy state of AB so that a transition may take place without a large alternation of the positions and momenta of the nuclei. A radiationless transition from the continuum nuclear state of AB^- to the bound nuclear state of AB may then cause the ejection of the outer electron. This, however, is not a very probable mechanism.

Now if the electronic states of colliding system (A,B^-) merge into some excited states of AB^- [Fig. 1(a)] or if the molecule AB does not have an electron affinity in the ground state [Fig. 1(b)], the situation becomes more complicated. The interaction potential of A and B^- must in this case intersect with the potential curve of AB at some distance of approach say R_c; there are usually several such intersection distances arising from the splitting of the interaction potential. Clearly, after A and B^- approach each other more closely than R_c, auto-ionization may occur, since the system lies above the ground state of AB and is involved therefore in configuration interaction with the continuum[14] $AB+e$. This then gives rise to a complex potential for the interaction of A and B^- at distances smaller than R_c. The real parts of the interaction potential are shown in Fig. 1 by the dashed curves. The imaginary parts of the interaction potential which account for the emission and absorption interactions come from the nonstationary nature of the electronic motion. These imaginary potentials are quantitatively the half-widths of the electronic states of AB^- and give the probability of auto-ionization. Thus, as soon as the colliding system is closer than R_c, the process of associative detachment may occur due to the imaginary parts of the potential which allow the system to eject the electron and hence to decay back into a lower molecular state of AB.

In general the situation is however not so clear cut, since there are a number of reaction paths available to

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[13] E. P. Wigner and E. Witmer, Z. Physik 51, 859 (1928).

[14] U. Fano, Phys. Rev. 124, 1866 (1961); Nuovo Cimento 12, 156 (1935); O. K. Rice, J. Chem. Phys. 1, 375 (1933).

the reaction system, namely

$$A+B^- \to A+B^-, \tag{2.2}$$

$$\to A^-+B, \tag{2.3}$$

$$\to AB+e, \tag{2.4}$$

$$\to \text{etc.} \tag{2.5}$$

Each reaction path, when energetically becomes accessible, may be represented by a set of open channels. Hence, the set of channels corresponding to Eqs. (2.2) and (2.3) lead, respectively, to the scattering and the electron-transfer processes. The only set of channels which leads to the process of associative detachment is the set corresponding to Eq. (2.4). Equation (2.5) refers to other processes such as collisional ionization and detachment which are of importance at higher energies. Also possible are processes such as associative ionization and detachment when the ionization potential of A is smaller than the electron affinity of B. Thus to be rigorous we must treat all these competitive processes when they become energetically allowed so that the coupling effects may be properly accounted for. The relative importance of the coupling of other processes to associative detachment varies considerably. For instance, the coupling effects due to the electron-transfer channels may become very important in the case of $A=B$, but, on the other hand, may be neglected for cases in which the differences in electron affinities between A and B are large and the potential curves are far apart.

Since, in the colliding system, A and B^- approach each other slowly (at room temperature the relative velocity v_0 is approximately equal to 10^5 cm/sec), the leading interaction is then the inverse-fourth-power polarization potential

$$V(R) \cong -\alpha e^2/2R^4, \tag{2.6}$$

where α is the electric polarizability of A. It is well known that such a polarization potential is capable of giving an orbiting collision in which A and B^- orbit about each other.[15] Classically, the cross section for such collisions is given by

$$\sigma_c \cong (2\pi/v_0)(\alpha e^2/\mu)^{1/2}, \tag{2.7}$$

where v_0 is the relative velocity and μ is the reduced mass of the colliding system A and B^-. Crudely, we may picture the cross section σ for associative detachment is given by the cross section σ_c for orbiting collisions multiplied by the probability p that the system auto-ionizes, i.e.,

$$\sigma \cong \sigma_c p. \tag{2.8}$$

Obviously this model is not realistic, especially at higher energies. As well, this model neglects the effects of the short-range repulsive potential. Nevertheless it is of interest to estimate roughly the magnitude of the reaction cross section for associative detachment by using this model.

If we take the electric polarizability α and the reduced mass to be of the order of $10a_0^3$ and 10 proton masses, respectively, we obtain for σ_c at thermal velocity a value which is of the order of 10^{-14} cm^2 from Eq. (2.7). Hence, the cross section for associative detachment can be easily as large as the Bohr orbit πa_0^2 if we assume that the probability for auto-ionization of AB^- before it dissociates is of the order of 10^{-2}, a moderate estimation. It need hardly be stressed that little significance should be attached to these numbers, since they are given here merely to demonstrate that in certain, but by no means exceptional, cases, the cross section for associative detachment can be large. A quantum-mechanical formulation of the problem is given in the next section.

Before going into the discussion of shape and crossing effects of potential curves to the reaction system, we emphasize that what we mean by potential curves is merely the internuclear separation dependence of the electronic energy of the Born-Oppenheimer electronic states.[16] This should not be confused with the interaction potential of the reaction system, since the former is defined only for given stationary electronic states. However, if splitting of the interaction potential due to the local electric field along the internuclear axis is sufficiently large and if we assume that the reactions are localized in regions of internuclear separation of the molecular dimension, we may approximate the interaction potential by an appropriate potential curve which lies within the energy region of our consideration. (This is related to the adiabatic case.) If there are more than one such potential curves lying close to each other within the energy of our consideration, the interaction potential should then be approximated by an appropriate combination of all these potential curves. (This is related to the nonadiabatic case.) Strictly speaking, the Born-Oppenheimer electronic states of AB^- are not stationary in most cases, since they may auto-ionize. Thus only in the quasistationary sense is it meaningful to speak of potential curves for such auto-ionization states.

Returning now to the interaction potential, we examine first the effect of the shape of potential curves for states of AB^- on the profile of the cross section for associative detachment. Two typical cases may arise depending on whether the real parts of the complex potential of AB^- lying within the binding region of AB are repulsive or attractive (see Fig. 2). For the qualitative discussions here, we neglect the effect of imaginary parts of the potential and assume that the process is adiabatic. In the repulsive case the picture is very clear [Fig. 2(a)], since the usual nuclear overlap integral arising from the Franck-Condon principle can be ap-

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[15] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (John Wiley & Sons, Inc., New York, 1964).

[16] M. Born and J. R. Oppenheimer, Ann. Physik **84**, 457 (1927).

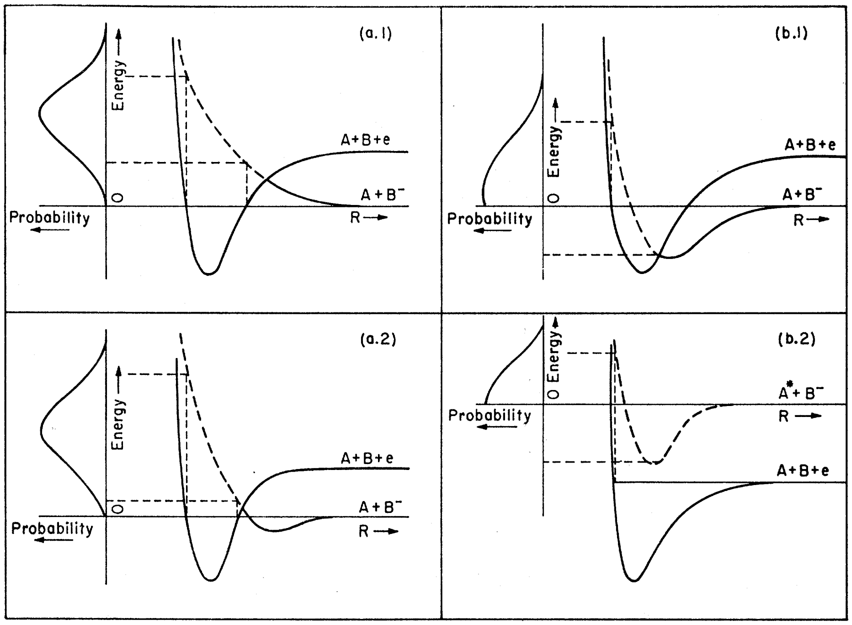

FIG. 2. Dependence of the transition probability profile on the relations between the shape of interaction potentials according to the Franck-Condon principle.

proximated by the reflection method.[17] This implies that the cross section would exhibit a peak with a width equivalent to the Franck-Condon width. In the attractive case the situation is different, since the lower portion (in the energy sense) of the reflected probability is absorbed by the quasistationary bound states of AB^- [Fig. 2(b)]. This will then result in a sharp rise of the cross section at low energies, indicating that at zero energy the cross section for associative detachment may become infinite as predicted by the classical model [Eq. (2.8)]. Theoretical studies concerning the behavior of the cross section at zero energy are desirable.

We now examine in some detail the crossing of potential curves between states of AB^- and $AB+e$. It is well known that two states with nearly the same energy in a certain approximate representation may become interacting with one another when the neglected small perturbation is explicitly considered in a higher approximation. This interaction will cause hybridization between the two states, and as a result the higher state will be displaced upwards and the lower state downwards (i.e., repelling each other) in the energy scale. The same phenomenon occurs for two potential curves, since they are actually stationary electronic states at various internuclear distances. Hence, two potential curves which at some nuclear distance have nearly the same energy in a certain approximation may in a higher approximation repel each other because of the additional perturbation considered in the higher approximation. This would be particularly so if the nuclei could be clamped at rest at the relevant internuclear distances.

However, in an actual case, the nuclei are moving relative to each other, so that the effect due to the additional perturbation may be weakened. Clearly, if the nuclei approach each other very rapidly in one of the states, they would not have sufficient time at the relevant internuclear distance to experience additional perturbation and to interact with the other state. The two potential curves then will not repel each other, and a diabatic transition may occur since in this case the potential curves effectively cross. Only when the nuclei approach each other very slowly does the internuclear distance change infinitesimally. Here the two potential curves may repel each other, and an adiabatic transition may take place. The latter case is known as the von Neumann and Wigner noncrossing rules[18] for electronic states of the same species.

It should be emphasized that, although the concept of potential curves is extremely useful (particularly in the case of diatomic molecules), potential curves are nevertheless theoretical intermediates which are meaningful only when the nuclei motion can be considered as taking place in the average field produced by the electrons at various internuclear distances. For the present case this then depends critically on the autoionization width of the compound state AB^-, since here the electronic state is only quasistationary (it is really a wave pocket). Now if the width Γ is sufficiently wide so that a changeover from AB^- to the state $AB+e$ will take place within a time $\tau=\hbar/\Gamma$ which is shorter than the time for a vibration of the nuclei, it is then hardly justifiable to consider the vibrational motion of the nuclei as taking place in the averaged field produced by the electrons in the AB^- state at various internuclear distances. In such a case the usefulness of the concept of potential curve for AB^- state is dubious.

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[17] E. U. Condon, Phys. Rev. **32**, 858 (1928); J. G. Winans and E. C. G. Stueckelberg, Proc. Natl. Acad. Sci. U. S. **14**, 867 (1928).

[18] J. von Neumann and E. P. Wigner, Z. Physik **30**, 467 (1929).

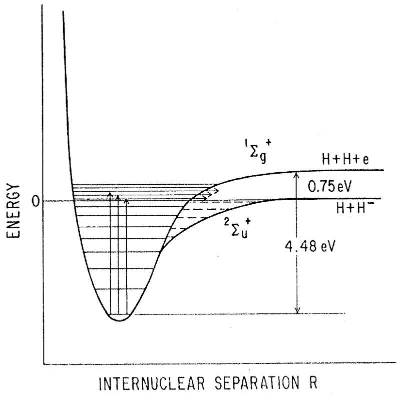

FIG. 3. Predissociation model for dissociative attachment in electron scattering by hydrogen molecules involving the lowest $^2\Sigma_u{}^+$ state of $H_2{}^-$.

This does not imply that one cannot define an interaction potential depending only on the nuclear coordinates but rather that the potential so defined would not reproduce the actual nuclear motion satisfactorily.

The above remarks are relevant to the lowest $^2\Sigma_u{}^+$ resonant state of $H_2{}^-$ which has a calculated width of about 4.5 eV with a minimum energy of about 1.75 eV lying above the ground $^1\Sigma_g{}^+$ state of H_2.[19] These results seem to suggest that the concept of potential curve for the lowest $^2\Sigma_u{}^+$ state is not very useful except at large internuclear distances where the system becomes more stable against auto-ionization. It might even be argued, assuming the calculated magnitude of width is correct,[20] that since the $^2\Sigma_u{}^+$ state of $H_2{}^-$ has a width of 4.5 eV and will decay in less than 10^{-16} sec, the changeover from the $^2\Sigma_u{}^+$ state to the $H_2(^1\Sigma_g{}^+)+e$ state becomes so rapid that the constituent nuclei will hardly even move. Hence, the averaged field in which the nuclear motion actually takes place is more realistically represented by the potential curve generated by the $H_2(^1\Sigma_g{}^+)+e$ state rather than that generated by the $^2\Sigma_u{}^+$ state of $H_2{}^-$.

The formation and decay of the $^2\Sigma_u{}^+$ $H_2{}^-$ state merely act as a distortion so that nuclear transitions may be induced in the averaged field of $H_2(^1\Sigma_g{}^+)+e$ state. Dissociative attachment may then occur, in the presence of a visiting electron, by nuclear excitation to states which lie near and above the threshold[21] of about 3.73 eV and accompanied by predissociation[22] of these states due to their interaction with the continuum nuclear state of $H+H^-$ (see Fig. 3). Since the cross section for vibrational excitation and dissociative attachment has been measured to be, respectively,[8,23] of the order of 10^{-17} and 10^{-21} cm^2 at the relevant energy region (around 4 eV), we may deduce that the probability of predissociation is of the order of 10^{-2} to 10^{-3}, allowing a factor of 10 to 100 for the decrease in magnitude of the vibrational excitation cross section for the excitation to higher vibrational states ($v \gtrsim 9$) which are capable of predissociation. For D_2 the nuclear states lying near the threshold are of much higher vibrational quantum number ($v \gtrsim 13$) than those of H_2, and subsequently, the vibrational excitation cross section can be easily further reduced by a factor of 10 or more going from H_2 to D_2. This then constitutes a possible explanation for the observed abnormal isotope effects[8] in comparison with dissociative attachment at other energy regions. This model also predicts a large temperature dependence for the onset of the cross section, since the probability for vibrational excitation depends strongly on the initial distribution of the H_2 nuclear states. This temperature dependence can be examined experimentally.

We conclude the physical description of the collisional processes in this section by commenting on the interaction of potential curves between different states of the compound ion AB^-. Such interactions are of importance in studying the problem of electron transfer and have been discussed in some detail by Lichten[24] in connection with resonant[25] electron-transfer problems. The essentially new features encountered in the present problem are the phenomenon of damping[26] due to electron emission and the phenomenon of overlapping interactions. The latter phenomenon may arise whenever the real parts of the potential curves come closer than their corresponding widths (which are twice the imaginary parts of the complex potential), since then the AB^- states become overlapping resonant states and are strongly coupled. This point will be further discussed in Sec. IV.3.

III. THEORY FOR MULTICHANNEL COLLISION

We adopt here the treatment for multichannel rearrangement collision recently formulated by Chen[27] using projection operators suggested by Feshbach.[28] We assume that the collision system (A,B^-) has only three sets of open channels, namely the set of scattering chan-

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[19] J. N. Bardsley, A. Herzenberg, and F. Mandl, *Abstract of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965), p. 359; J. N. Bardsley, thesis, University of Manchester, 1965 (unpublished).

[20] The experimentally deduced width (Ref. 8) is also of the same order (>1.5 eV). It should be noted that the equation used in determining the width is valid, however, only when the width is much smaller than the relative kinetic energy of the atom and ion [see Eqs. (4.25) and (4.28)]. For the system in question, neither the width is small nor is the relative velocity between H and H^- large.

[21] It is the energy difference between the dissociative energy of H_2 (4.48 eV) and the electron affinity of H (0.75 eV).

[22] G. Hertzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950), Chap. VII.

[23] G. J. Schulz, Phys. Rev. **135**, A988 (1964).

[24] W. Lichten, Phys. Rev. **131**, 229 (1963); **139**, A27 (1965); F. P. Ziemha and A. Russek, *ibid.* **115**, 922 (1959); R. P. Marchi and F. T. Smith, *ibid.* **139**, A1025 (1965).

[25] It should be noted that by resonance here (and only here) we specifically refer to the cases in which the initial (before electron transfer) and the final (after electron transfer) states are degenerate. This should not be confused with resonances in scattering and reaction theory in which intermediate compound states are formed.

[26] Damping may also occur because of the mixing in additional states, so that interference between degenerate states is destroyed, and because of the lack of exact degeneracy between initial and final states.

[27] J. C. Y. Chen, Phys. Rev. **152**, 1454 (1966).

[28] H. Feshbach, Ann. Phys. (N. Y.) **5**, 357 (1958); **19**, 287 (1962); L. Fonda and R. G. Newton, *ibid.* **10**, 490 (1960).

nels, and two sets of rearrangement channels for associative detachment and electron transfer respectively. These are quite realistic situations for cases in which A and B^- represent atoms and atomic ions, since collisional detachment and ionization which are of importance only at high energies can be considered as special cases belonging to the above three sets of channels.[29] For molecular cases, transmutations and fragmentations of the molecules or of the molecular ions may take place. In principle, we should then include, according to their relative importance, the corresponding sets of channels in our consideration.

Let p_1, p_2, and p_3 denote projectors which project, respectively, onto the scattering, associative-detachment, and electron-transfer sets of open channels and which satisfy the idempotent and the orthogonal relation

$$p_j p_{j'} = p_j \delta_{jj'}, \quad j, j' = 1, 2, 3 \tag{3.1}$$

where $\delta_{jj'}$ is the delta function. Then it is obvious that p_j is capable of projecting out the jth set of open channels from the total reaction wave function Υ. Asymptotically, we thus have

$$p_1\Upsilon \underset{q_1\to\infty}{\longrightarrow} \sum_{\lambda=1}^{N'} \varphi_m{}^{(a)}(\mathbf{r}_a{}')\varphi_{m'}{}^{(b)}(\mathbf{r}_b{}')\left\{e^{i\mathbf{k}_1\cdot\mathbf{q}_1}\delta_{\lambda 1} + f_\lambda(\hat{k}_1,\hat{q}_1)\frac{e^{ik_{1\lambda}q_1}}{q_1}\right\}, \quad \lambda=(m,m'), \tag{3.2}$$

$$p_2\Upsilon \underset{q_2\to\infty}{\longrightarrow} \sum_{\mu=1}^{M} \Psi_n(\mathbf{r}',\mathbf{R})\chi_{nv}(\mathbf{R})g_\mu{}^{(2)}(\hat{k}_1,\hat{q}_2)\frac{e^{ik_{1\mu}q_2}}{q_2}, \quad \mu=(n,v), \tag{3.3}$$

$$p_3\Upsilon \underset{q_3\to\infty}{\longrightarrow} \sum_{\nu=1}^{N} \psi_{m'}{}^{(a)}(\mathbf{r}_a)\psi_m{}^{(b)}(\mathbf{r}_b)g_\nu{}^{(3)}(\hat{k}_1,\hat{q}_3)\frac{e^{ik_{1\nu}q_3}}{q_3}, \quad \nu=(m',m), \tag{3.4}$$

where the q_j's are the channel coordinates, $\{\varphi_m{}^{(a)},\varphi_{m'}{}^{(b)}\}$ are, respectively, the wave functions of A and B^- with $\mathbf{r}_a{}'$ and $\mathbf{r}_b{}'$ denoting collectively the coordinates of the atomic electrons, $\{\Psi_n,\chi_{nv}\}$ are, respectively, the electronic and nuclear wave functions of the molecule AB with $\mathbf{R}$ denoting the nuclear coordinate and $\mathbf{r}'$ denoting collectively the coordinates of the molecular electrons, and finally $\{\psi_{m'}{}^{(a)},\psi_m{}^{(b)}\}$ are, respectively, the wave functions of A^- and B with $\mathbf{r}_a$ and $\mathbf{r}_b$ denoting collectively the coordinates of the atomic electrons. The functions f_λ, $g_\mu{}^{(2)}$, and $g_\nu{}^{(3)}$ are, respectively, the transition amplitudes for scattering, associative-detachment, and electron-transfer processes. For the case $A=B$, the interference due to the corresponding asymptotic degenerate states can be appropriately accounted for[30] by rewriting the asymptotic expression for $p_1\Upsilon$ and $p_3\Upsilon$ in terms of the symmetrical and antisymmetrical combinations of the f's and $g^{(3)}$'s.

The projection operators P and Q which project onto the open and the closed channels of the Hilbert space, respectively, can now be constructed in terms of the projectors

$$P=\sum_{j=1}^{3} p_j, \quad Q=1-P=1-\sum_{j=1}^{3} p_j. \tag{3.5}$$

The projectors are not necessarily Hermitian, but their sum must be Hermitian so that the P is a projection operator. The non-Hermitian character of the projectors comes from the fact that there is mixing of amplitudes among different sets of channels. The projectors become Hermitian at large channel coordinates (i.e., at $q_j\to\infty$), since asymptotically the flux at various channels is well defined. The explicit expressions for the projectors are derived in Sec. V. Note however that our discussion in this section involves only the existence of the projectors.

When the projection operators P and Q are utilized, the Schrödinger equation

$$\{H-E\}\Upsilon=0 \tag{3.6}$$

may be rewritten as[28]

$$(\mathcal{H}-E)P\Upsilon=0 \tag{3.7}$$

with

$$\mathcal{H}=P\left\{H+HQ\frac{1}{E-QHQ}QH\right\}P. \tag{3.8}$$

If P does not include all the open channels, E in Eq. (3.8) should be replaced by $E+i\eta$ with $\eta^+\to 0$. It has been shown by Feshbach[28] that resonances come from the bound-state solution of the Q-projected Hamiltonian QHQ:

$$\{QHQ-\mathcal{E}_\alpha{}'\}Q\Phi_\alpha=0, \tag{3.9}$$

where $\mathcal{E}_\alpha{}'$ is a quasistationary approximation of the resonance energy.

For the sake of clarity, we consider the case of an isolated resonance. Utilizing Eqs. (3.9), (3.1), and (3.5), we may rewrite the effective Schrödinger equation [Eq. (3.7)] as

$$\{E-\mathcal{H}_{p_j}{}^{(1)}\}p_j\Upsilon=p_jHQ\Phi_\alpha\Lambda_\alpha+\sum_{j'\neq j}^{3}\mathcal{H}_{p_jp_{j'}}{}^{(1)}p_{j'}\Upsilon, \tag{3.10}$$

where

$$\mathcal{H}_{p_j}{}^{(1)}\equiv\mathcal{H}_{p_jp_j}{}^{(1)}, \tag{3.11}$$

$$\mathcal{H}_{p_jp_{j'}}{}^{(1)}=p_j\mathcal{H}p_{j'}-p_jHQ|\Phi_\alpha\rangle \times(E-\mathcal{E}_\alpha{}')^{-1}\langle\Phi_\alpha|QHp_{j'}, \tag{3.12}$$

$$\Lambda_\alpha=\sum_{j=1}^{3}\Lambda_{\alpha_j}=\sum_{j=1}^{3}\frac{1}{E-\mathcal{E}_\alpha{}'}\langle\Phi_\alpha|QHp_j|p_j\Upsilon\rangle. \tag{3.13}$$

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[29] Namely scattering excitation and electron transfer into continuum states and decaying of AB^- into repulsive and predissociative states of AB.

[30] H. S. W. Massey and R. A. Smith, Proc. Roy. Soc. (London) **A142**, 142 (1933); N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Clarendon Press, Oxford, 1965), 3rd ed., Chap. XIX.

Equation (3.10) may be solved formally[27] for $p_j\Upsilon$:

$$p_j\Upsilon = p_j v^{(+)}\delta_{1j} + \frac{1}{a_j}\Big\{\tilde{p}_j HQ\Phi_\alpha\Lambda_\alpha + \sum_{j'\neq j}^{3} \mathcal{H}_{p_jp_{j'}}{}^{(1)} p_{j'}\psi\Big\}, \quad (3.14)$$

with

$$a_j = E - \mathcal{H}_{p_j}{}^{(1)} + i\eta, \quad (3.15)$$

$$p_j\psi = p_j v^{(+)}\delta_{1j} + \frac{1}{a_j}\sum_{j'\neq j}^{3} \mathcal{H}_{p_jp_{j'}}{}^{(1)} p_{j'}\psi, \quad (3.16)$$

$$\tilde{p}_j = p_j + \sum_{j'\neq j}^{3} \mathcal{H}_{p_jp_{j'}} \frac{1}{a_{j'}} \tilde{p}_{j'}, \quad (3.17)$$

where $p_j v^{(+)}$ is the appropriate solution of

$$\{E - \mathcal{H}_{p_j}{}^{(1)}\} p_j v^{(+)} = 0, \quad (3.18)$$

and $\tilde{p}_j$ defined by Eq. (3.17) is an operator series.

Note that the formal solution given by Eq. (3.14) is decoupled with respect to the direct and resonance components of the reaction wave function $p_j\Upsilon$ in the jth set of channels. The various contributions to the transition matrix $\mathcal{T}_j$ for the scattering and rearrangement collisions can now be obtained from the asymptotic behavior of $p_j\Upsilon$.

$$\mathcal{T}_j = \mathcal{T}_j{}^{(p)}\delta_{1j} + \mathcal{T}_j{}^{(d)} + \mathcal{T}_j{}^{(r)}, \quad (3.19)$$

with

$$\mathcal{T}_j{}^{(d)} = \sum_{j'\neq j}^{3} \langle p_j v^{(-)} | \mathcal{H}_{p_jp_{j'}}{}^{(1)} | p_{j'}\psi\rangle, \quad (3.20)$$

$$\mathcal{T}_j{}^{(r)} = \langle p_j v^{(-)} | \tilde{p}_j HQ | \Lambda_\alpha Q\Phi_\alpha\rangle, \quad (3.21)$$

where $\mathcal{T}_j{}^{(p)}$ is the potential scattering amplitude arising from Eq. (3.25), where $\mathcal{T}_j{}^{(d)}$ is the direct scattering or rearrangement amplitude arising from channel coupling and where finally $\mathcal{T}_j{}^{(r)}$ is the resonance transition amplitude arising from compound-state formation.

Substitution of $p_j\Upsilon$ from Eq. (3.14) back into the definition of Λ_α given by Eq. (3.13) yields the expression for determining the resonance structure function. We then have

$$\Lambda_\alpha = \Big[\langle\Phi_\alpha|QHp_1|p_1v^{(+)}\rangle + \sum_{j=1}^{3}\sum_{j'\neq j}^{3}\langle\Phi_\alpha|QHp_{j'}\frac{1}{a_j}\mathcal{H}_{p_jp_{j'}}{}^{(1)}|p_{j'}\psi\rangle\Big] \Big/ \Big[E - \mathcal{E}_\alpha' - \sum_{j=1}^{3}\langle\Phi_\alpha|QHp_j\frac{1}{a_j}\tilde{p}_jHQ|\Phi_\alpha\rangle\Big], \quad (3.22)$$

where the matrix elements in the denominator of Eq. (3.22) give rise to a complex shift in the quasistationary resonance energy $\mathcal{E}_\alpha'$. We will return to these equations in the next section and discuss in more detail that how, in the framework of the Born-Oppenheimer separation approximation, the resonance structure function may be defined for a fixed nuclear configuration. Substitution of Λ_α into Eq. (3.21) yields for the resonance transition matrix

$$\mathcal{T}_j{}^{(r)} = \frac{\langle p_jv^{(-)}|p_jHQ|\Phi_\alpha\rangle\langle\Phi_\alpha|QHp_1|p_1v^{(-)}\rangle}{E-\mathcal{E}_\alpha+\frac{1}{2}i\Gamma_\alpha} + \sum_{j'\neq j}^{3}\frac{\langle p_jv^{(-)}|\mathcal{H}_{p_jp_{j'}}{}^{(1)}(1/a_{j'})p_{j'}HQ|\Phi_\alpha\rangle\langle\Phi_\alpha|QHp_1|p_1v^{(+)}\rangle}{E-\mathcal{E}_\alpha+\frac{1}{2}i\Gamma_\alpha}$$
$$+\sum_{j'\neq 1}^{3}\frac{\langle p_jv^{(-)}|p_jHQ|\Phi_\alpha\rangle\langle\Phi_\alpha|QHp_{j'}(1/a_{j'})\mathcal{H}_{p_{j'}p_j}|p_1v^{(+)}\rangle}{E-\mathcal{E}_\alpha+\frac{1}{2}i\Gamma_\alpha}+\cdots, \quad (3.23)$$

with

$$\mathcal{E}_\alpha + \tfrac{1}{2}i\Gamma_\alpha \equiv \mathcal{E}_\alpha' + \sum_{i=1}^{3}\langle\Phi_\alpha|QHp_j\frac{1}{a_j}\tilde{p}_jHQ|\Phi_\alpha\rangle, \quad (3.24)$$

where we have used Eqs. (3.16) and (3.17) to carry out the expansion. Similar expansion for direct transition matrix $\mathcal{T}_j{}^{(d)}$ can be obtained from Eq. (3.20) using Eq. (3.16).

The cross section for the scattering or reaction is given in terms of the transition matrix

$$\sigma_j = \left(\frac{\mu_i\mu_j}{4\pi^2}\right)^2 \frac{k_{jf}}{k_{1i}} \int |\mathcal{T}_j|^2 d\Omega_j, \quad (3.25)$$

where μ_j is the reduced mass in the jth set of channels and $d\Omega_j$ is the solid angle of the exit flux in the jth set of channels. Since the transition matrix satisfies the reciprocity relation, for specific sets of initial and final states (denoted by i and f, respectively), we have the well-known relation of detailed balancing[31]

$$k_{jf}{}^2\sigma_j(i\to f) = k_{ji}{}^2\sigma_j{}^{(-1)}(f\to i), \quad (3.26)$$

where the superscript (-1) denotes the corresponding reverse process. However, there may exist degeneracies in both initial and final states; the detailed-balancing relation must be accordingly modified. If we assert that all states of the same energy are occupied with equal probability in equilibrium, we then have[32]

$$g_{jf}k_{jf}{}^2\sigma_j = g_{ji}k_{ji}{}^2\sigma_j{}^{(-1)} \quad (3.27)$$

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[31] See, for example, A. Messiah, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Chap. XIX.

[32] E. Fermi, *Nuclear Physics*, edited by J. Orear, A. H. Rosenfeld and R. A. Schluter (University of Chicago Press, Chicago, Illinois, 1950), Chap. VIII.

for the cross sections which are averaged over all the initial degenerated states and summed over all the final degenerated states. The g_j's in Eq. (3.27) are the state degeneracy factors. This then enables us to obtain the cross section from its reverse which could be of great usefulness for associative detachment since detailed cross-section measurement for this process is not available except for its reverse process namely dissociative attachment.

Now most available experimental information concerning associative detachment is in the form of rate coefficient, it is instructive to examine the relations between cross section and rate coefficient. For a theoretical prediction of the rate coefficient, a knowledge of the probability of atoms and ions in their various initial states is necessary in addition to a knowledge of the cross section. If the experimental setup is such that the population of the various initial states for the reactants is in thermal equilibrium, then the rate coefficient can be easily formulated in terms of the appropriately thermal-averaged[33] cross section $\bar{\sigma}_j$.

$$\bar{\sigma}_j = (Z_A Z_{B^-})^{-1} \sum_{L,m,L',m'}{}' g_{ji}(L,L')\sigma_j \times \exp\{-[\epsilon_{mL}{}^{(a)} + \epsilon_{m'L'}{}^{(b)}]/KT\}, \tag{3.28}$$

with

$$g_{ji}(L,L') = g_s g_{s'}(2L+1)(2L'+1), \tag{3.29}$$

where $\epsilon_{mL}{}^{(a)}$ and $\epsilon_{m'L'}{}^{(b)}$ are, respectively, the energies for states of A and B^-; L and L' are, respectively, the total angular momenta of A and B^-; K and T are, respectively, the Boltzmann constant and temperature of the system; Z_A and Z_{B^-} are, respectively, the partition functions[33] for A and B^-; $g_s g_{s'}$ is the product of spin degeneracies of A and B^-, and finally the prime on the summation sign indicates a sum over all the allowed final states. The rate coefficient κ_j is then given by[33]

$$\kappa_j = \left(\frac{\mu_j}{9\pi KT}\right)^{3/2} \int e^{-E/KT} \bar{\sigma}_j(E) v_1 d\mathbf{v}_1, \tag{3.30}$$

where v_1 is the relative velocity of the reactants A and B^-.

The rate coefficient for the reverse process $\kappa_j{}^{(-1)}$ can be written down in a similar manner from the cross section obtained from Eq. (3.27) by using, of course, a different thermal averaging. In the case of dissociative attachment (i.e., the reverse process of associative detachment, $j=2$), the thermal-averaged cross section takes the expression

$$\bar{\sigma}_2{}^{(-1)} = Z_{AB}{}^{-1} \sum_{n,v,N}{}' g_{2f}(N)\sigma_2{}^{(-1)} e^{-[\epsilon_{nv}+\epsilon_N]/KT} \tag{3.31}$$

with

$$g_{2f} = 2(2N+1)g_s{}', \tag{3.32}$$

where $Z_{AB}{}^{-1}$ is the partition function, N is the rotational quantum number, the ϵ_N's are the rotational energies, the ϵ_{nv}'s are the vibronic energies, and finally $g_s{}'$ is the spin degeneracy of the molecule AB. Recently, a striking temperature dependence has been observed in connection with the onset of dissociative-attachment cross section.[34] It is of interest to investigate this temperature dependence of the cross section onset by using Eq. (3.32).

IV. APPLICATION TO REARRANGEMENT COLLISIONS

1. Direct Associative Detachment

The process of associative detachment may proceed directly as given by Eq. (3.20) without the formation of intermediate compound states. To consider such a case, let us assume for the moment that the set of electron-transfer channels ($j=3$) is closed (see Fig. 2), we then have from Eqs. (3.20) and (3.16)

$$\mathcal{T}_2{}^{(d)} = \langle p_2 v^{(-)} | \mathcal{H}_{p_2 p_1}{}^{(1)} | p_1 \psi \rangle, \tag{4.1}$$

with

$$p_1\psi = p_2 v^{(+)} + (1/a_1)\mathcal{H}_{p_1 p_2}{}^{(1)} p_2 \psi, \tag{4.2}$$

$$p_2\psi = (1/a_2)\mathcal{H}_{p_2 p_1}{}^{(1)} p_1 \psi, \tag{4.3}$$

where the numbering for subscript j is clear from Eqs. (3.2) to (3.4). Eliminating $p_2\psi$ we obtain from Eqs. (4.2) and (4.3) the Lippmann-Schwinger equation for $p_1\psi$,

$$p_1\psi = p_1 v^{(+)} + (1/a_1)\mathcal{H}_{p_1 p_2}{}^{(1)} (1/a_2)\mathcal{H}_{p_2 p_1}{}^{(1)} p_1 \psi, \tag{4.4}$$

which may be rewritten in the Schrödinger form

$$\{\mathcal{H}_{p_1}{}^{(1)} + \mathcal{H}_{p_1 p_2}{}^{(1)} (1/a_2)\mathcal{H}_{p_2 p_1}{}^{(1)} - E\} p_1 \psi = 0. \tag{4.5}$$

With $p_1\psi$ determined from Eq. (4.5), the transition matrix for direct associative detachment can then be obtained from Eq. (4.1).

It is however instructive to examine Eq. (4.5) in the framework of the Born-Oppenheimer separation approximation.[16] We write for $p_1\psi$,

$$p_1\psi = \psi_\beta(\mathbf{r},\mathbf{R}) \Xi_\beta(\mathbf{R}), \tag{4.6}$$

with

$$\langle \psi_\beta(\mathbf{r},\mathbf{R}) | p_1 | \psi_\beta(\mathbf{r},\mathbf{R}) \rangle_{\mathbf{r}} = 1 \text{ for all } R, \tag{4.7}$$

where **r** denotes collectively all the electron coordinates, **R** is the coordinate of the nuclei and the integral indicated by the brackets with subscript **r** in Eq. (4.7) is over all the electronic coordinates. Substitution of Eq. (4.6) into Eq. (4.5) yields

$$\{K_{\mathbf{R}} + V_\beta(\mathbf{R}) + \Delta_\beta(\mathbf{R}) - \tfrac{1}{2} i \Gamma_\beta(\mathbf{R})\} \Xi_\beta(\mathbf{R}) = E \Xi_\beta(\mathbf{R}), \tag{4.8}$$

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[33] See, for example, L. Landau and E. Lifschitz, *Statistical Physics* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1958), Chap. XIX.

[34] W. L. Fite, R. T. Brachman, and U. R. Henderson, *Abstract of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, 1965* (Science Bookcrafters, Hastings-on-Hudson, New York, 1965), p. 100; R. F. Stebbings, M. A. Fineman, J. W. McGowan, B. A. Turner, and F. A. Wolf, Electronic and Ionic Reactions in Atmospheric Gases, Defense Atomic Support Agency Report DASA-GA-6699, 1965 (unpublished).

with

$$V_\beta(\mathbf{R})=\langle\psi_\beta|\mathcal{H}_{p_1}{}^{(1)}-K_{\mathbf{R}}p_1|\psi_\beta\rangle-(1/2\mu)\times\langle\psi_\beta|(\nabla_{\mathbf{R}}{}^2p_1\psi_\beta)\rangle, \quad (4.9)$$

$$\Delta_\beta(\mathbf{R})=\mathrm{Re}\langle\psi_\beta|\mathcal{H}_{p_1p_2}{}^{(1)}(1/a_2)\mathcal{H}_{p_2p_1}{}^{(1)}|\psi_\beta\rangle, \quad (4.10)$$

$$\Gamma_\beta(\mathbf{R})=-2\ \mathrm{Im}\langle\psi_\beta|\mathcal{H}_{p_1p_2}{}^{(1)}(1/a_2)\mathcal{H}_{p_2p_1}{}^{(1)}|\psi_\beta\rangle, \quad (4.11)$$

where μ is the reduced mass of the nuclei and $K_{\mathbf{R}}$ is the relative nuclear kinetic-energy operator. Equation (4.8) describes the nuclear motion when the electronic motions of the two sets of channels (i.e., the scattering and associative-detachment sets of channels) are strongly coupled. Because of this coupling, the constituent nuclei experience a complex potential. We emphasize that this is a one-step transition[35] as shown in Fig. 2 and should not be confused with resonance reaction in which intermediate compound states are formed. (The latter case will be treated in subsection IV.2.)

Now utilizing the completeness properties of the spherical harmonics, we may always expand $\Xi_\beta(\mathbf{R})$ as

$$\Xi_\beta(\mathbf{R})=\sum_{J,M}\frac{1}{R}\{\eta_{JM}{}^{(\beta)}+i\zeta_{JM}{}^{(\beta)}(R)\}Y_{JM}(\hat{R}). \quad (4.12)$$

Equation (4.8) may be rewritten as a pair of coupled equations

$$\left\{\frac{d^2}{dR^2}-\frac{J(J+1)}{R^2}+2\mu[E-V_\beta(R)-\Delta_\beta(R)]\right\}\eta_{JM}{}^{(\beta)}(R)=\mu\Gamma_\beta(R)\zeta_{JM}{}^{(\beta)}(R), \quad (4.13\text{a})$$

$$\left\{\frac{d^2}{dR}-\frac{J(J+1)}{R^2}+2\mu[E-V_\beta(R)-\Delta_\beta(R)]\right\}\zeta_{JM}{}^{(\beta)}(R)=-\mu\Gamma_\beta(R)\eta_{JM}{}^{(\beta)}(R), \quad (4.13\text{b})$$

where we have assumed that the complex potential is a function of radial coordinate R only. For continuum solutions of Eq. (4.8) we impose the boundary conditions that the solutions vanish at $R=0$ and have the asymptotic forms

$$\eta_{JM}{}^{(\beta)}(R)\underset{R\to\infty}{\longrightarrow}k_\beta{}^{-1}\cosh\delta_{\beta J}{}^{(2)}\times\sin(k_\beta R-\tfrac{1}{2}J\pi+\delta_{\beta J}{}^{(1)}), \quad (4.14\text{a})$$

$$\zeta_{JM}{}^{(\beta)}(R)\underset{R\to\infty}{\longrightarrow}k_\beta{}^{-1}\sinh\delta_{\beta J}{}^{(2)}\times\cos(k_\beta R-\tfrac{1}{2}J\pi+\delta_{\beta J}{}^{(1)}). \quad (4.14\text{b})$$

Clearly Eq. (4.14) implies that

$$\xi_{\beta J}(R)=\eta_{JM}{}^{(\beta)}+i\zeta_{JM}{}^{(\beta)}\underset{R\to\infty}{\longrightarrow}k_\beta{}^{-1}\times\sin(k_\beta R-\tfrac{1}{2}J\pi+\delta_{\beta J}), \quad (4.15)$$

where

$$\delta_{\beta J}=\delta_{\beta J}{}^{(1)}+i\delta_{\beta J}{}^{(2)} \quad (4.16)$$

is a complex phase shift.

Note that though the rotational motion of the nuclei in a diatomic molecule behaves essentially like a simple rotator, the spherical harmonics do not, however, always provide a realistic representation of the rotational states. In an actual molecule there are a number of electrons revolving about the two nuclei, and in many cases this may yield a nonzero net resultant electronic angular momentum along the internuclear axis (denoted by Λ). The net angular momentum then causes the nuclei to deviate from the simple rotator behavior so that the rotational quantum number L is no longer a good quantum number. In addition, this electron orbital motion provides a net current around the axis and generates a magnetic field parallel to the axis. This magnetic field will then be coupled with electron spins. For molecules of light atoms, the electron spins may combine first to form a total spin angular momentum S which is virtually unaffected by the internuclear electric field. If we neglect the multiplet splitting due to the coupling of the spin angular momentum with the magnetic field of the current (resulting from electron orbital motion along the internuclear axis) and regard S as a good quantum number, the rotational motion of the nuclei may be more realistically represented by a symmetric-top rotator.[22] Expansions of $\Xi_\beta(\mathbf{R})$ should then be carried out in terms of the orthonormal set of symmetric-top wave function.[36] In a more rigorous treatment, the effect of nuclear spin should also be considered.

In accordance with the assumption made in Eq. (4.13) that $V(R)$ and $\Gamma(R)$ are spherically symmetric, we may utilize the axial symmetry about k_β and write[37]

$$\Xi_\beta(\mathbf{R})=\frac{4\pi}{R}\sum_{J,M_J}i^Je^{i\delta_{\beta J}}\xi_{\beta J}(R)Y_{JM_J}(\hat{R})Y_{JM_J}{}^*(\Omega_i). \quad (4.17)$$

This then permits us to write for the cross section for direct associative detachment as

$$\sigma_2{}^{(d)}=\frac{\mu_2\mu_1}{4\pi^2}\frac{k_{2f}}{k_{1i}}\int|\sum_J i^Je^{i\delta_{\beta J}}\tau_J|^2d\Omega_2, \quad (4.18)$$

with

$$\tau_J=4\pi\sum_{M_J}\langle p_2v^{(-)}|\mathcal{H}_{p_2p_1}{}^{(1)}|R^{-1}\xi_{\beta J}(R)Y_{JM_J}(\hat{R})\psi_\beta(\mathbf{r},\mathbf{R})\rangle\times Y_{JM_J}{}^*(\Omega_i) \quad (4.19)$$

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[35] For the corresponding reverse process—dissociative attachment—the same observation applies, since the process proceeds by direct capturing of the projectile electron into a repulsive state of the target molecule. It is a one-step transition. Note that the final repulsive state is in the open-channel space. The fact that the final state may auto-ionize merely means that back couplings with the set of scattering channel are of importance. This implies that one need not evoke the resonance theory for treating direct dissociative attachment of the Franck-Condon type [see Ref. 10]. Only in the fixed nuclear configuration approximation, one may treat the auto-ionization state as an intermediate resonance state. (See Sec. III of Ref. 10a.)

[36] F. Reiche and H. Rademacher, Z. Physik **39**, 444 (1926); **41**, 453 (1927); R. de L. Kronig and I. I. Rabi, Phys. Rev. **29**, 262 (1927); D. M. Dennison, *ibid.* **28**, 318 (1926).

[37] See for example, T.-Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962), p. 6.

where it is understood that the expression for the cross section is averaged over the initial degenerate states. For a given J, the cross section becomes

$$\sigma_2^{(d)} \cong e^{-2\delta_{\beta J}^{(2)}} \frac{\mu_2\mu_1}{4\pi^2} \frac{k_{2f}}{k_{1i}} \int |\tau_J|^2 d\Omega_2. \quad (4.20)$$

We observe that the cross section is directly proportional to a energy-dependent exponential factor.

This factor was first discussed by Holstein[38] in interpreting the process of dissociative attachment and was later derived independently by Bardsley *et al.*[11,39] The physical significance of this factor can be made apparent by examining the phase shift as a function of R. Now if we treat the radial nuclear motion semiclassically, we have [see Eqs. (4.13) to (4.16)]

$$\xi_{\beta J}(R) = K_\beta(R)^{-1/2} \exp\left[\pm i \int^R K_\beta(R')dR'\right]$$

with

$$K_\beta(R) = \{2\mu[E - U(R) + \tfrac{1}{2} i \Gamma_\beta(R)]\}^{1/2}, \quad (4.21)$$

$$U(R) = V_\beta(R) + \Delta_\beta(R) + J(J+1)(2\mu R^2)^{-1}.$$

Consideration of the requirement that $\xi_{\beta J}(R)$ vanishes at $R=0$ leads to[40]

$$\xi_{\beta J}(R) \cong K_\beta(R)^{-1/2} \sin\left\{\tfrac{1}{4}\pi - D_\beta^{(+)}(R_0) + i D_\beta^{(-)}(R_0) + \int_{R_0}^R K_\beta(R')dR'\right\}, \quad (4.22)$$

with

$$D_\beta^{(\pm)}(R_0) = -\tfrac{1}{6}\sqrt{2}\mu\Gamma(R_0)^{3/2} \left\{ \left(\frac{dU_\beta}{dR} \pm \frac{1}{2}\frac{d\Gamma_\beta}{dR}\right) \Big/ \left[\left(\frac{dU_\beta}{dR}\right)^2 + \frac{1}{4}\left(\frac{d\Gamma_\beta}{dR}\right)^2\right]\right\}_{R=R_0}, \quad (4.23)$$

where $J(J+1)$ in $K_\beta(R)$ is replaced by $(J+\frac{1}{2})^2$, the $D_\beta^{(\pm)}(R_0)$ arises from the imaginary part of the potential at R_0, and R_0 is the turning point of the nuclei in the complex potential.

The complex phase shift can now be obtained from the asymptotic behavior of Eq. (4.22).

$$\delta_{\beta J} = (J+\tfrac{1}{2})\tfrac{1}{2}\pi - kR_0 - D_\beta^{(+)}(R_0) + i D_\beta^{(-)}(R_0) + \lim_{R\to\infty} \int_{R_0}^R [K_\beta(R) - k] dR, \quad (4.24)$$

where $k = (2\mu E)^{1/2}$. If we expand $K_\beta(R)$, assuming that $\Gamma_\beta(R)$ is small,[11,12] and retain only the first two terms; we obtain

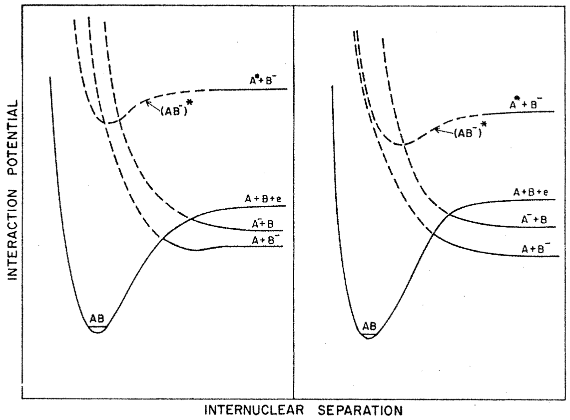

FIG. 4. Examples of intermediate compound states of the reaction system (A,B^-). The compound state may decay either by auto-ionization into $AB+e$ or by predissociation into A^-+B or $A+B^-$.

$$\delta_{\beta J}^{(1)} \cong (J+\tfrac{1}{2})\tfrac{1}{2}\pi - kR_0 - D_\beta^{(+)}(R_0) + \lim_{R\to\infty} \int_{R_0}^R [\mu v(R') - k] dR', \quad (4.25)$$

$$\delta_{\beta J}^{(2)} \cong D_\beta^{(-)}(R_0) + \lim_{R\to\infty} \frac{1}{2} \int_{R_0}^R \frac{\Gamma(R')dR'}{v(R')}, \quad (4.26)$$

with

$$v(R) = \{(2/\mu)[E - V_\beta(R) - \Delta_\beta(R)] - [(J+\tfrac{1}{2})/(\mu R)]^2\}^{1/2}, \quad (4.27)$$

where $v(R)$ is the relative velocity of the nuclei at separation R. Since $dR/v(R)$ is the time taken by the nuclei to separate by a distance dR, the exponential factor therefore takes the expression

$$\exp[-2\delta_{\beta J}^{(2)}] \cong \exp\left\{-2D_\beta^{(-)}(R_0) - \lim_{R\to\infty} \int_{t(R_0)}^{t(R)} \Gamma[t(R')] dt(R')\right\} \quad (4.28)$$

which is just the probability of survival of the ion as the nuclei move apart. It has been referred to by Bardsley *et al.* as survival probability. We note that the J dependence of the survival probability is of importance in connection with selection rules. This will be discussed in some detail in a subsequent communication.[41]

2. Resonance Associative Detachment

Associative detachment may take place indirectly in which intermediate compound states are formed as discussed in Sec. III. For simplicity we will consider

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[38] T. Holstein, Phys. Rev. **84**, 1073 (1951).

[39] See also, Yu. N. Demkov, Phys. Letters **15**, 235 (1965).

[40] R. E. Langer, Phys. Rev. **51**, 669 (1937).

[41] J. C. Y. Chen and J. L. Peacher (to be published).

the case of isolated resonance. A typical situation of this kind is illustrated in Fig. 4. If the collision system (A,B^-) approach each other with an energy just below the excitation energy for exciting A up to A^*, the colliding partners may merge into a quasistationary bound state of $(AB^-)^*$. Since this state crosses (or lies very close to) the repulsive state of AB^- and is imbedded in the continuum $AB+e$ (Fig. 4), it may predissociate or autoionize. The competitive predissociation process will then interfere with the process of auto-ionization which stabilizes the process of associative detachment. One would therefore expect that this interference will give rise to structures in the cross section for associative detachment. In addition, if the width of the compound state $(AB^-)^*$ is narrow in comparison with its vibrational spacings, one would also expect the vibrational structure to appear in the cross section.[42] Recently such structure has been observed[43] for the hydrogen system in the energy range between 8 to 12 eV in the reverse process of associative detachment–dissociative attachment. This seems to be consistent with the vibrational resonance seen by Kuyatt *et al.*[44] in the (H_2,e) scattering system at the same energy region.

The transition matrix for resonance associative detachment is given by Eq. (3.21) in which the resonance-structure function Λ_α is given by Eq. (3.13). For reasonable long-lived compound states so that the Born-Oppenheimer separation approximation[16] is valid, we may write for the compound state $Q\Phi_\alpha$,

$$Q\Phi_\alpha=\varphi_\alpha(\mathbf{r},\mathbf{R})X_\alpha(\mathbf{R}), \tag{4.29}$$

with

$$\langle\varphi_\alpha(\mathbf{r},\mathbf{R})|Q|\varphi_\alpha(\mathbf{r},\mathbf{R})\rangle_{\mathbf{r}}=1,\ \text{for all } R, \tag{4.30}$$

where φ_α is the quasistationary representation of the electronic wave function of the compound state. Utilizing Eq. (3.9) with the help of Eqs. (4.29) and (4.30), Eq. (3.13) may be rewritten in the operator form

$$\Lambda_\alpha(\mathbf{R})=\sum_{j=1}^{3}\frac{1}{E-K_{\mathbf{R}}-V_\alpha(\mathbf{R})}\langle\varphi_\alpha|QHp_j|p_j\Upsilon\rangle_{\mathbf{r}} \tag{4.31}$$

with

$$V_\alpha(\mathbf{R})=\langle\varphi_\alpha|QH_eQ|\varphi_\alpha\rangle-(1/2\mu)\langle\varphi_\alpha|(\nabla_R{}^2Q\varphi_\alpha), \tag{4.32}$$

where $H_e=H-K_R$ is the electronic Hamiltonian of the system.

Substitution of $p_j\Upsilon$ from Eq. (3.14) back into the expression for $\Lambda_\alpha(\mathbf{R})$ given by Eq. (4.31) yields the equation for determining the resonance structure function for a fixed nuclei configuration

$$\left\{E-K_{\mathbf{R}}-V_\alpha(\mathbf{R})-\sum_{j=1}^{3}\langle\varphi_\alpha|QHp_j\frac{1}{a_j}\tilde{p}_jHQ|\varphi_\alpha\rangle\right\}\Lambda_\alpha(R)$$
$$=\mathfrak{F}_\alpha(\mathbf{R}), \tag{4.33}$$

where the inhomogeneous source function is

$$\mathfrak{F}_\alpha(\mathbf{R})=\langle\varphi_\alpha|QHp_1|p_1v^{(+)}\rangle_{\mathbf{r}}$$
$$+\sum_{j=1}^{3}\sum_{j'\neq j}^{3}\langle\varphi_\alpha|QHp_j\frac{1}{a_j}\mathcal{H}_{p_jp_{j'}}{}^{(1)}|p_{j'}\psi\rangle. \tag{4.34}$$

Now if we substitute $\tilde{p}_j$ as given by Eq. (3.17) into Eq. (4.34), we obtain

$$\{E-K_{\mathbf{R}}-V_\alpha(\mathbf{R})-\Delta_\alpha'(\mathbf{R})-\mathcal{W}_\alpha(\mathbf{R})+\tfrac{1}{2}i\Gamma_\alpha'(\mathbf{R})\}\Lambda_\alpha(\mathbf{R})$$
$$=\mathfrak{F}_\alpha(\mathbf{R}) \tag{4.35}$$

with

$$\Delta_\alpha'(\mathbf{R})-\tfrac{1}{2}i\Gamma_\alpha'(\mathbf{R})=\sum_{j=1}^{3}\{\Delta_{\alpha j}'(\mathbf{R})-\tfrac{1}{2}i\Gamma_{\alpha j}'(R)\}$$
$$=\sum_{j=1}^{3}\langle\varphi_\alpha|QHp_j\frac{1}{a_j}p_jHQ|\varphi_\alpha\rangle \tag{4.36}$$

$$\mathcal{W}_\alpha(\mathbf{R})=\sum_{j=1}^{3}\sum_{j'\neq j}^{3}\langle\varphi_\alpha|QHp_j\frac{1}{a_j}\mathcal{H}_{p_jp_{j'}}{}^{(1)}\tilde{p}_{j'}HQ|\varphi_\alpha\rangle, \tag{4.37}$$

where $\Delta_{\alpha j}'(\mathbf{R})$ is the energy shift from the quasistationary approximation arising from the coupling of φ_α with the jth set of open channels, where $\Gamma_{\alpha j}'(R)$ is the decaying width of the compound state φ_α into the jth set of open channels and where finally $\mathcal{W}_\alpha$ is the complex energy shift arising from multiple back and forth couplings between channels. The complex energy shift is usually very small.

Equation (4.35) describes the nuclear motion when the electronic states of A and B^- merge into that of the compound system. Because of the quasistationary nature of the electronic state, the constituent nuclei experience a complex potential. An approximate equation similar to Eq. (4.35) has been derived[11] for dissociative attachment using Kapur-Peierls formalism. Here the equation is derived without evoking the concept of channel radius, the decoupling of the electronic angular states or the explicit expression for the projectors.

Solving Eq. (4.35) for $\Lambda_\alpha(\mathbf{R})$, we have

$$\Lambda_\alpha(\mathbf{R})=[1/b_\alpha(\mathbf{R})]\mathfrak{F}_\alpha(\mathbf{R}), \tag{4.38}$$

with

$$b_\alpha(\mathbf{R})=E-K_{\mathbf{R}}-U_\alpha(\mathbf{R}), \tag{4.39}$$

$$U_\alpha(\mathbf{R})=\{V_\alpha(\mathbf{R})+\Delta_\alpha'(\mathbf{R})+\mathrm{Re}[\mathcal{W}_\alpha(R)]\}$$
$$-\tfrac{1}{2}i\{\Gamma_\alpha'(R)-2\,\mathrm{Im}[\mathcal{W}_\alpha(R)]\}. \tag{4.40}$$

Substitution of $\Lambda_\alpha(\mathbf{R})$ into Eq. (3.21) yields the expansion similar to Eq. (3.23)

$$\mathcal{T}_j{}^{(r)}=\big\langle\langle p_jv^{(-)}|p_jHQ|\varphi_\alpha\rangle_{\mathbf{r}}$$
$$\times[b_\alpha(\mathbf{R})]^{-1}\langle\varphi_\alpha|QHp_1|p_1v^{(+)}\rangle_{\mathbf{r}}\big\rangle_{\mathbf{R}}+\cdots, \tag{4.41}$$

where the integrals indicated by the outer most brackets are over the nuclear coordinates **R** as indicated by the subscript **R**. Within the energy region of resonance, the

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[42] See, for example, J. C. Y. Chen, Phys. Rev. **146**, 61 (1966).

[43] T. Sharp (private communication).

[44] C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, J. Chem. Phys. 44, 437, 440 (1966).

transition matrix may be approximate by its first (leading) term. In this approximation the coupling effects due to other sets of channels do not appear [except in a very trivial way they appear in the propagator $b_\alpha(\mathbf{R})^{-1}$].

It is worthwhile to mention that the resonance-transition matrices for associative detachment or dissociative attachment, for the scattering of electrons by molecules or of atoms by ions, and for electron transfer in atom-ion collisions are identical in functional form. Independent of the initial or final scattering or reaction state, for each isolated resonance there exists a unique complex propagator for the nuclear states which does not depend on individual channels but on all the open channels as a whole. The collective dependence of the propagator on all channels comes from the total width $\Gamma_\alpha'(\mathbf{R})$, the total energy shift $\Delta_\alpha'(\mathbf{R})$, and the over all complex shift $W_\alpha(\mathbf{R})$ since they are the sum of partial contributions from each set of channels [see Eqs. (4.36) and (4.37)].

For overlapping resonances, Eq. (4.35) becomes a set of coupled equations, and the propagator for the nuclear states becomes much more complicated. The number of coupled equations is equal to the number of overlapping resonances α_0. Hence

$$\sum_{\alpha'=1}^{\alpha_0}\left\{[E-K_R-V_\alpha(\mathbf{R})]\delta_{\alpha\alpha'}\right.$$
$$\left.-\sum_{j=1}^{3}\langle\varphi_\alpha|QHp_j\frac{1}{a_j}\tilde{p}HQ|\varphi_\alpha\rangle\right\}\Lambda_{\alpha'}(\mathbf{R})=\mathfrak{F}_\alpha(\mathbf{R}),\quad(4.42)$$
$$\alpha=1,2,\cdots,\alpha_0.$$

From examination of Eq. (4.42), it is apparent that the coupling potentials among different resonant states are complex. We mentioned in Sec. II that overlapping interaction may occur whenever the real parts of the potential curves [i.e., the real parts of the potential in Eq. (4.42)] for states of AB^- come closer than their corresponding widths [i.e., twice the imaginary parts of the potential in Eq. (4.42)]. Recently, the problem of interaction of potential curves for states of AB^- was studied[45] in the framework of Kapur-Peierls resonance theory. In this study, the overlapping interactions were, however, not considered.

3. Electron Transfer

Finally, in this subsection we consider the electron-transfer rearrangement collision. For the case of electron transfer involving negative ions, the coupling with associative-detachment set of channels is of importance, since the coupling would cause electron emission and would therefore result in a damping in the electron-transfer probability as mentioned in Sec. II. This effect does not, however, appear in electron transfer involving positive ions, except for special cases. We demonstrate here that such damping due to electron emission may be expressed in terms of complex potentials for the nuclear motion.

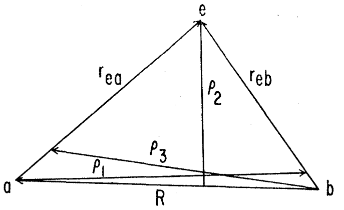

FIG. 5. Active-electron representation of the coordinates for the reaction system (A,B^-).

From Eq. (3.20) we have for direct electron transfer the transition matrix

$$\mathcal{T}_3^{(d)}=\langle p_3v^{(-)}|\mathcal{H}_{p_3p_1}^{(1)}|p_1\psi\rangle$$
$$+\langle p_3v^{(-)}|\mathcal{H}_{p_3p_2}^{(1)}|p_2\psi\rangle,\quad(4.43)$$

where the second term which is small in comparison with the first term accounts for the contribution to the electron transfer coming from the recapture of the electron. The corresponding reaction wave functions are given by Eq. (3.16).

$$\begin{aligned}p_1\psi&=p_1v+(1/a_1)\{\mathcal{H}_{p_1p_2}^{(1)}p_2\psi+\mathcal{H}_{p_1p_3}^{(1)}p_3\psi\},\\p_2\psi&=(1/a_2)\{\mathcal{H}_{p_2p_1}^{(1)}p_1\psi+\mathcal{H}_{p_2p_3}^{(1)}p_3\psi\},\\p_3\psi&=(1/a_3)\{\mathcal{H}_{p_3p_1}^{(1)}p_1\psi+\mathcal{H}_{p_3p_2}^{(1)}p_2\psi\}.\end{aligned}\quad(4.44)$$

On eliminating $p_2\psi$, we obtain a pair of coupled equations for $p_1\psi$ and $p_3\psi$, which may be written in the Schrödinger form

$$\{E-\mathcal{H}_{p_1}^{(1)}-\mathcal{H}_{p_1p_2}^{(1)}(1/a_2)\mathcal{H}_{p_2p_1}^{(1)}\}p_1\psi$$
$$=\{\mathcal{H}_{p_1p_3}^{(1)}+\mathcal{H}_{p_1p_2}^{(1)}(1/a_2)\mathcal{H}_{p_2p_3}^{(1)}\}p_3\psi,\quad(4.45\mathrm{a})$$

$$\{E-\mathcal{H}_{p_3}^{(1)}-\mathcal{H}_{p_3p_2}^{(1)}(1/a_2)\mathcal{H}_{p_2p_3}^{(1)}\}p_3\psi$$
$$=\{\mathcal{H}_{p_3p_1}^{(1)}+\mathcal{H}_{p_3p_2}^{(1)}(1/a_2)\mathcal{H}_{p_3p_1}^{(1)}\}p_1\psi.\quad(4.45\mathrm{b})$$

This provides an exact description of direct electron transfer between atoms and negative ions. The essentially new feature of these pair of coupled equations from those for electron transfer involving positive ions[46] is in the presence of complex potentials. It becomes more apparent if one carries out the Born-Oppenheimer separation approximation for $p_1\psi$ and $p_3\psi$ similar to that carried out in Eqs. (4.6) to (4.11).

Electron-transfer process may, of course, also take place involving compound states as intermediates. The analysis is essentially the same as that given in IV.2 and will not be repeated here.

V. CONSTRUCTION OF THE PROJECTION OPERATOR

The asymptotic expressions for the projected wave functions $p_1\Upsilon$, $p_2\Upsilon$, and $p_3\Upsilon$ are given by Eqs. (3.2) to

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[45] F. Mandl, Proc. Phys. Soc. (London) 87, 871 (1966).

[46] D. R. Bates and R. McCarroll, Advan. Phys. (Phil. Mag. Suppl.) 14, 521 (1965); J. C. Y. Chen, Brookhaven National Laboratory Report, BNL 9148, 1965 (unpublished).

(3.4) where the channel coordinates that were used in these equations are illustrated in Fig. 5. For simplicity only the active electron (i.e., the outer electron to be detached or transferred) and the two heavy nuclei a and b are explicitly shown in the figure; the remaining electrons are omitted. Making use of the geometric relations (Fig. 5)

$$\boldsymbol{\varrho}_1=\mathbf{R}-\mu_b\mathbf{r}_{eb},\quad \mu_b=m_e/(M_b+m_e)\,, \tag{5.1}$$

$$\boldsymbol{\varrho}_3=\mathbf{R}+\mu_a\mathbf{r}_{ea},\quad \mu_a=m_e/(M_a+m_e)\,, \tag{5.2}$$

and the fact that the φ's and the ψ's are bounded in $\mathbf{r}_{ea}$ and $\mathbf{r}_{eb}$ respectively, we obtain for $\boldsymbol{\varrho}_1$ and $\boldsymbol{\varrho}_3$ in Eqs. (3.2) and (3.4) the asymptotic expression[47]

$$\rho_1=|\boldsymbol{\varrho}_1|\rightarrow R-\mu_b\hat{R}\cdot\mathbf{r}_{eb}+O(R^{-1})\,, \tag{5.3}$$

$$\rho_3=|\boldsymbol{\varrho}_3|\rightarrow R+\mu_a\hat{R}\cdot\mathbf{r}_{ea}+O(R^{-1})\,. \tag{5.4}$$

Substitution of Eqs. (5.1), (5.3), and (5.4) back into Eqs. (3.2) and (3.4) reveals the definitions for the projectors p_1 and p_3

$$p_1\Upsilon=|\hat{\varphi}_1'\rangle F_1'(\mathbf{R})+\sum_{\lambda}^{N'}|\hat{\varphi}_\lambda\rangle F_\lambda(\mathbf{R})\,, \tag{5.5}$$

$$p_3\Upsilon=\sum_{\nu}^{N}|\hat{\psi}_\nu\rangle G_\nu^{(3)}(\mathbf{R})\,, \tag{5.6}$$

with

$$F_1'(\mathbf{R})\underset{R\to\infty}{\longrightarrow}e^{i\mathbf{k}_1\cdot\mathbf{R}}\,, \tag{5.7}$$

$$F_\lambda(\mathbf{R})\underset{R\to\infty}{\longrightarrow}f_\lambda(\hat{k}_1\cdot\hat{R})(e^{ik_{1\lambda}R}/R)\,, \tag{5.8}$$

$$G_\nu^{(3)}(\mathbf{R})\underset{R\to\infty}{\longrightarrow}g_\nu^{(3)}(\hat{k}_1\cdot\hat{R})(e^{ik_{1\nu}R}/R)\,, \tag{5.9}$$

where $|\hat{\varphi}_1'\rangle$, $|\hat{\varphi}_\lambda\rangle$, and $|\hat{\psi}_\nu\rangle$ are the recoil states

$$|\hat{\varphi}_1'\rangle=\mathcal{A}\{\varphi_1^{(a)}(\mathbf{r}_a')\varphi_1^{(b)}(\mathbf{r}_b')e^{-i\mu_b\mathbf{k}_1\cdot\mathbf{r}_{eb}}\}\,, \tag{5.10}$$

$$|\hat{\varphi}_\lambda\rangle=\mathcal{A}\{\varphi_m^{(a)}(\mathbf{r}_a')\varphi_{m'}^{(b)}(\mathbf{r}_b')e^{-i\mu_bRk_{1\lambda}\cdot\mathbf{r}_{eb}}\}\,,\qquad \lambda=(m,m')\,, \tag{5.11}$$

$$|\hat{\psi}_\nu\rangle=\mathcal{A}\{\psi_{m'}^{(a)}(\mathbf{r}_a)\psi_m^{(b)}(\mathbf{r}_b)e^{i\mu_aRk_{1\nu}\cdot\mathbf{r}_{ea}}\}\,,\qquad \nu=(m',m)\,. \tag{5.12}$$

It can be seen by substituting Eqs. (5.7) to (5.9) back into Eqs. (5.5) and (5.6) that Eqs. (5.5) and (5.6) asymptotically gives the desired expression for the scattering and electron-transfer channels as required by Eqs. (3.2) and (3.4).

For associative-detachment channels, we may solve for each given nuclear configuration $\chi_{n\nu}(\mathbf{R})$, a Born-Oppenheimer electronic scattering state $\hat{\Psi}_{n\nu}(\mathbf{r},\mathbf{R})$ such that

$$\{H_e-E_e\}\hat{\Psi}_{n\nu}(\mathbf{r},\mathbf{R})=0\,, \tag{5.13}$$

$$\hat{\Psi}_\mu(\mathbf{r},\mathbf{R})\underset{q_2\to\infty}{\longrightarrow}\Psi_n(\mathbf{r}',\mathbf{R})\left\{g_\mu^{(2)}(\mathbf{R},\hat{k}_1\cdot\hat{q}_2)\frac{e^{ik_{1\mu}q_2}}{q_2}\right\}\,,\qquad \mu=(n,v)\,, \tag{5.14}$$

where $\mathbf{r}=(\mathbf{r}',\mathbf{q}_2)$ and H_e is the total electronic Hamiltonian of the reaction system (A,B^-). The scattering state $\hat{\Psi}_\mu$ which may be normalized in a box can be determined by constructing a projection operator which projects onto the molecular state $\Psi_n(\mathbf{r}',\mathbf{R})$ of AB molecule.[10a,48] This then permits us to define the projector for associative-detachment p_2

$$p_2\Upsilon=\sum_{\mu}^{M}\hat{\Psi}_\mu(\mathbf{r},\mathbf{R})\chi_\mu(\mathbf{R})\,, \tag{5.15}$$

where the $\chi_{n\nu}(\mathbf{R})$'s are, of course, bounded in $\mathbf{R}$. Substitution of the asymptotic expression for $\hat{\Psi}_\mu$ into the expression for $p_2\Upsilon$ yields the desired asymptotic expression [Eq. (3.3)] for $q_2\to\infty$. This can be easily seen from Eq. (3.14).

Mathematically, the definition for the projectors given by Eqs. (5.5), (5.6), and (5.15) are equivalent to require the projectors to satisfy the following equations:

$$\langle\hat{\varphi}_1'|1-p_1-p_2-p_3|\Upsilon\rangle=0\,, \tag{5.16a}$$

$$\langle\hat{\varphi}_\lambda|1-p_1-p_2-p_3|\Upsilon\rangle=0\,, \tag{5.16b}$$

$$\langle\hat{\Psi}_\mu|1-p_1-p_2-p_3|\Upsilon\rangle=0\,, \tag{5.16c}$$

$$\langle\hat{\psi}_\nu|1-p_1-p_2-p_3|\Upsilon\rangle=0\,. \tag{5.16d}$$

Equations (5.16) may be rewritten as a set of coupled equations for the functions F_1', F_λ, χ_μ, and G_ν. Since we have constrained both the scattering and electron-transfer channel coordinates to be $\mathbf{R}$ by introducing the recoil states [Eqs. (5.10) to (5.12)] and since we have utilized the Born-Oppenheimer electronic scattering states for the associative detachment, the set of coupled equations can easily be solved for F_1', F_λ, χ_μ, and G_ν in terms of inner products involving Υ. Substitution of the solutions so obtained back into Eqs. (5.5), (5.6), and (5.15) yields immediately the desired projectors. Such an algebraic manipulation can in general be carried out in terms of matrix notations. For the sake of clarity we consider here a simple case in which only the lowest channels in each set of channels are open.

When the definitions for the projectors given by Eqs. (5.5), (5.6), and (5.15) are utilized, Eqs. (5.6) may be rewritten for the case $N=N'=M=1$ as follows:

$$\begin{aligned}
F_1'(\mathbf{R})+a_{12}F_1(\mathbf{R})+a_{13}(\mathbf{R})\chi_1(\mathbf{R})+a_{14}(\mathbf{R})G_1^{(3)}(\mathbf{R})&=U'(\mathbf{R})\,,\\
a_{12}^*F_1'(\mathbf{R})+F_1(\mathbf{R})+a_{23}(\mathbf{R})\chi_1(\mathbf{R})+a_{24}(\mathbf{R})G_1^{(3)}(\mathbf{R})&=U(\mathbf{R})\,,\\
a_{13}^*(\mathbf{R})F_1'(\mathbf{R})+a_{23}^*(\mathbf{R})F_1(\mathbf{R})+\chi_1(\mathbf{R})+a_{34}(\mathbf{R})G_1^{(3)}(\mathbf{R})&=V(\mathbf{R})\,,\\
a_{14}^*(\mathbf{R})F_1'(\mathbf{R})+a_{24}^*(\mathbf{R})F_1(\mathbf{R})+a_{34}^*(\mathbf{R})\chi_1(\mathbf{R})+G_1^{(3)}(\mathbf{R})&=W(\mathbf{R})\,,
\end{aligned} \tag{5.17}$$

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[47] J. C. Y. Chen and M. H. Mittleman, Ann. Phys. (N. Y.) **37**, 264 (1966).

[48] We take occasion to note that in the treatment of Ref. 10a the scattering amplitude is obtained by averaging the fixed-nuclear scattering amplitude [Eq. (2.8) of Ref. 10a] over the nuclear state χ obtained from the coupled equation [Eq. (3.17) of Ref. 10a] in solving for the dissociative-attachment amplitude.

with

$$a_{12}=\langle\hat{\varphi}_1'|\hat{\varphi}_1\rangle,\quad a_{13}(\mathbf{R})=\langle\hat{\varphi}_1'|\hat{\Psi}_1\rangle,\quad a_{14}(\mathbf{R})=\langle\hat{\varphi}_1'|\hat{\psi}_1\rangle, \tag{5.18}$$

$$a_{23}(\mathbf{R})=\langle\hat{\varphi}_1|\hat{\Psi}_1\rangle,\quad a_{24}(\mathbf{R})=\langle\hat{\varphi}_1|\hat{\psi}_1\rangle,\quad a_{34}(\mathbf{R})=\langle\hat{\Psi}_1|\hat{\psi}_1\rangle,$$

$$U'(\mathbf{R})=\langle\hat{\varphi}_1'|\Upsilon\rangle,\quad U(\mathbf{R})=\langle\hat{\varphi}_1|\Upsilon\rangle,\quad V(\mathbf{R})=\langle\hat{\Psi}_1|\Upsilon\rangle,\quad W(\mathbf{R})=\langle\hat{\psi}_1|\Upsilon\rangle, \tag{5.19}$$

where the integrals indicated by the brackets in Eqs. (5.18) and (5.19) are over coordinates that are common on both sides in the brackets.

Solving Eqs. (5.7) we obtain

$$\begin{aligned}
F_1'(\mathbf{R})&=\gamma(\mathbf{R})\{b_1U'(\mathbf{R})+c_{12}U(\mathbf{R})+c_{13}V(\mathbf{R})+c_{14}W(\mathbf{R})\},\\
F_1(\mathbf{R})&=\gamma(\mathbf{R})\{c_{21}U'(\mathbf{R})+b_2U(\mathbf{R})+c_{23}V(\mathbf{R})+c_{24}W(\mathbf{R})\},\\
\chi_1(\mathbf{R})&=\gamma(\mathbf{R})\{c_{31}U'(\mathbf{R})+c_{32}U(\mathbf{R})+b_3V(\mathbf{R})+c_{34}W(\mathbf{R})\},\\
G_1^{(3)}(\mathbf{R})&=\gamma(\mathbf{R})\{c_{41}U'(\mathbf{R})+c_{42}U(\mathbf{R})+c_{43}V(\mathbf{R})+b_4W(\mathbf{R})\},
\end{aligned} \tag{5.20}$$

with

$$\gamma(\mathbf{R})=\{1-|a_{34}(\mathbf{R})|^2\}\{c_{12}(\mathbf{R})c_{21}(\mathbf{R})-b_1(\mathbf{R})b_2(\mathbf{R})\}^{-1}, \tag{5.21}$$

$$b_i(\mathbf{R})=|a_{jk}|^2+|a_{kl}|^2+|a_{lj}|^2-2R_e[a_{jk}a_{kl}a_{lj}]-1, \qquad 5.22)$$

$$c_{ij}(\mathbf{R})=a_{ij}(1-|a_{kl}|^2)+a_{ik}(a_{kl}a_{lj}-a_{kj})+a_{il}(a_{lk}a_{kj}-a_{lj});\quad i,\ j,\ k,\ l=1,\ 2,\ 3 \text{ or } 4 \text{ but } i\neq j\neq k\neq l, \tag{5.23}$$

where the overlap integrals, i.e., $a_{13}(\mathbf{R})$, $a_{14}(\mathbf{R})$, $a_{23}(\mathbf{R})$, $a_{24}(\mathbf{R})$, and $a_{34}(\mathbf{R})$ of Eq. (5.18), approach to zero exponentially as their argument R become large. It can be easily shown by substituting the asymptotic expression for Υ into U', U, V, and W [see Eq. (5.19)] that $\chi_1(\mathbf{R})$ is bounded and that F_1', F_1, and $G_1^{(3)}$ satisfy the asymptotic expressions given by Eqs. (5.7), (5.8), and (5.9), respectively.

Substitution of F_1' and F_1 back into Eq. (5.5), $G_1^{(2)}$ back into Eq. (5.15) and $G_1^{(3)}$ back into Eq. (5.6) yields, respectively, the projector for the scattering channels

$$\begin{aligned}
p_1=\gamma\{&|\hat{\varphi}_1'\rangle b_1\langle\hat{\varphi}_1'|+|\hat{\varphi}_1\rangle b_2\langle\hat{\varphi}_1|+|\hat{\varphi}_1'\rangle c_{12}\langle\hat{\varphi}_1+|\hat{\varphi}_1\rangle c_{21}\langle\hat{\varphi}_1'|+|\hat{\varphi}_1'\rangle c_{13}\langle\hat{\Psi}_1|+|\hat{\varphi}_1\rangle c_{23}\langle\hat{\Psi}_1|\\
&+|\hat{\varphi}_1'\rangle c_{14}\langle\hat{\psi}_1|+|\hat{\varphi}_1\rangle c_{24}\langle\hat{\psi}_1|\},
\end{aligned} \tag{5.24}$$

the projector for the associative-detachment channels

$$p_2=\gamma\{|\hat{\Psi}_1\rangle b_3\langle\hat{\Psi}_1|+|\hat{\Psi}_1\rangle c_{31}\langle\hat{\varphi}_1'|+|\hat{\Psi}_1\rangle c_{32}\langle\hat{\varphi}_1|+|\hat{\Psi}_1\rangle c_{34}\langle\hat{\psi}_1|\} \tag{5.25}$$

and the projector for the electron-transfer channels

$$p_3=\gamma\{|\hat{\psi}_1\rangle b_4\langle\hat{\psi}_1|+|\hat{\psi}_1\rangle c_{41}\langle\hat{\varphi}_1'|+|\hat{\psi}_1\rangle c_{42}\langle\hat{\varphi}_1|+|\hat{\psi}_1\rangle c_{43}\langle\hat{\Psi}_1|\}. \tag{5.26}$$

It is straightforward to show that the projectors given by the above equations are idempotent and mutually orthogonal, $p_jp_{j'}=p_j\delta_{jj'}$, as required by Eq. (3.1). The projectors are asymptotically Hermitian, $p_j(R\rightarrow\infty)=p_j^\dagger(R\rightarrow\infty)$, since

$$\begin{aligned}
&p_1\xrightarrow[R\rightarrow\infty]{}\frac{1}{1-|a_{12}|^2}\{|\varphi_1'\rangle\langle\varphi_1'|+|\varphi_1\rangle\langle\varphi_1|-|\varphi_1'\rangle a_{12}\langle\varphi_1|-|\varphi_1\rangle a_{12}^*\langle\varphi'_1|\},\\
&p_2\xrightarrow[R\rightarrow\infty]{}|\hat{\Psi}_1\rangle\langle\hat{\Psi}_1|,\quad p_3\xrightarrow[R\rightarrow\infty]{}|\hat{\psi}_1\rangle\langle\hat{\psi}_1|.
\end{aligned} \tag{5.27}$$

The appropriate projection operator P for the open channels is then obtained by sum over the projectors.

$$P=\sum_{j=1}^{3}p_j=P^2. \tag{5.28}$$

By inspection of Eqs. (5.24) to (5.26), it is apparent that P is Hermitian even though the projectors are Hermitian only asymptotically. This then completes the demonstration of the construction of the projection operator.

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