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Absolute cross sections from the "boomerang model" for resonant electron-molecule scattering

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The boomerang model is used to calculate *absolute* cross sections near the $^2\Pi_g$ shape resonance in e-N_2 scattering. The calculated cross sections are shown to satisfy detailed balancing. The exchange of electrons is taken into account. A parametrized complex-potential curve for the intermediate N_2^- ion is determined from a small part of the experimental data, and then used to calculate other properties. The calculations are in good agreement with the absolute cross sections for vibrational excitation from the ground state, the absolute cross section $v = 1 \rightarrow 2$, and the absolute total cross section.

I. INTRODUCTION

A. Objective

Perhaps the most thoroughly studied of all resonances in electron-molecule scattering at energies of a few electron volts occurs at about 2 eV in e-N_2 collisions.[1] It plays a major role in the pumping of the CO_2-N_2 laser,[2] and in the slowing of electrons and the transport of energy in the upper atmosphere.[3] The resonance arises from the temporary capture of an electron into the lowest vacant orbital in the N_2 molecule; it is a "shape resonance," in the sense that the target molecule provides a potential well, but does not become excited (except for a minor polarization). The extra electron enters and departs by tunneling through a barrier due to a centrifugal potential.

Up to now, almost all observations on the 2-eV resonance in e-N_2 scattering experiments have dealt with inelastic processes, the excitation of vibrations,[4] and rotation.[5] Recently, it has become possible[6] to detect *superelastic* collisions, in which the energy of the bombarding electron increases by a vibrational quantum. Despite the absence of measurements, the cross sections are often needed in calculations on gas lasers[7] and in atmospheric processes.[8] The cross sections may be calculated[9] with the "boomerang model," which corresponds to a lifetime of the transitory N_2^- ion so short that the nuclei have time for only a single vibrational cycle before the extra electron departs. The object of this paper is to present new calculations with the boomerang model on both superelastic and inelastic processes in the resonance region. The cross sections are given in absolute magnitude. Comparison with experiment confronts absolute measured cross sections with absolute calculated cross sections. The theoretical discussion is restricted to the e-N_2 resonance; only minor changes are needed to modify the theory for other resonances.

The present calculations are an extension of earlier calculations[9] on the reaction

$$e + N_2 \rightarrow N_2^- \rightarrow N_2^* + e',$$

which fitted the energy dependence of the observed cross sections for the excitation of the lowest seven vibrationally excited states of N_2 from the ground state, but did not give the absolute magnitude; that calculation was based on a parametrized potential-energy curve for the N_2^- ion. The permissible values of all but one of the adjustable parameters are tied down almost completely by an *ab initio* calculation.[10] The one remaining parameter is a "correlation energy," which Krauss and Mies[10] adjusted to get the resonance appearing at the right energy. It turned out in Ref. 9 that the potential parameters needed to fit the observed cross sections are in excellent agreement with the *ab initio* calculation of Krauss and Mies, if their chosen value of the correlation energy was used. There are some differences in notation between this paper and Ref. 9; they are explained in the Appendix.

B. Obervations

The e-N_2 resonance was observed first in measurements of the total cross section,[11] with energy resolution too poor to observe vibrational structure. The first measurement with energy resolution good enough to detect vibrational structure and to record the excitation of individual vibrational states were done by Schulz[12] in 1962. Further measurements of vibrational excitation in $e + N_2$ scattering near 2 eV were published by Schulz[13] and by Ehrhardt and Willmann.[14] The experimental situation has been reviewed by Schulz,[1] most recently in 1976.

Measurements of the total cross section which detect vibrational structure have been done by Golden[15] and by Bonham and Kennerley.[16]

C. Previous calculations

The first calculations of e-N_2 scattering near the 2-eV resonance were done by Stier[17] in 1932 and Fisk[18] in 1936. They regarded the nuclei as fixed, and so began a long series of fixed-nucleus calculations, which is still being pursued. At the time Stier and Fisk did their calculations, the available experiments showed a strong resonance, about 1 eV wide, but there was no hint of vibrational structure.

For Stier and Fisk to treat the nuclei as fixed was consistent with the available experimental evidence on nuclear relaxation. The experimental picture changed drastically in 1962, when Schulz[12] demonstrated nuclear relaxation experimentally. He observed vibrational structure which had to be associated with the transient N_2^- ion formed at the resonance, because the peak positions and spacings bore no resemblance to the vibrational levels of the electronic ground state of the neutral N_2 molecule.

With Schulz's demonstration of nuclear relaxation, there arose a rift of opinion among theorists: one school[19-21] thought that the nuclear relaxation had to be built into the calculations, while another school[22-24] felt that the fixed-nucleus calculations could still somehow be rescued. A lively debate[25] between representatives of the two schools of thought took place in 1973, with Temkin for the fixed-nucleus school, and one of us for the relaxers. However, the rift of opinion has now been healed by a study[26] by Chandra and Temkin, in which they showed that only if the nuclei in the transient N_2^- are allowed to relax does one obtain oscillations in the energy dependence of the cross sections which resemble the experiments. Moreover, it has become clear from the good agreement between the *ab initio* calculations of Ref. 10 and the parameters needed to fit experiments in Ref. 9 that the method of Ref. 9 offers a way in which results from fixed-nucleus models can be incorporated in calculations with relaxing nuclei.

In 1962, as soon as the results of Schulz's experiment[12] were published, it was shown[19,20] that his observations could be reproduced fairly well in a calculation which took nuclear relaxation into account. At first, there was no simple physical picture of the origin of the striking regularities observed by Schulz, but such a picture was eventually supplied.[27] It is now called the "boomerang model," because the nuclei execute only a single vibrational cycle during the limited lifetime of the N_2^- ion. Later, in 1971, it was shown[9] that a calculation which rests on the essential physics of the boomerang picture gives a good fit of the energy dependence of the cross sections observed by Schulz.

In the "boomerang model,"[9,27] the incoming electron is supposed to be trapped in a quasistationary electronic state $\psi(q, \vec{R})$, where q stands for the totality of electronic coordinates and $\vec{R}$ for the coordinates of the nuclei. As any electron moves out, ψ decreases at first, either because the electron happens to be in a truly bound orbital, or because it happens to be in an orbital confined within a potential barrier; at large distances, ψ joins to outgoing waves, representing decay by autoionization. The state ψ has a finite decay rate $\Gamma(\vec{R})/\hbar$, which depends on the position of the nuclei. Such states are hardly novel. In 1928 Gamow[28] introduced the concept of the particle emitting unstable state in his treatment of the α decay of nuclei, and showed that the energy must be complex; the imaginary part is $-\frac{1}{2}\Gamma$. Ten years later, in 1938, Kapur and Peierls[29] used a complete set of particle-emitting states with complex energies to discuss resonance scattering in nuclei.

In the boomerang model, one supposes that the lifetime of ψ happens to be so short that the electron is usually emitted after the nuclei have executed about a single vibrational cycle. How this picture leads to the regularities observed by Schulz is explained in Refs. 9 and 27. There is now a good example of a contrasting case,[30,31] in which the lifetime against autoionization is much shorter, so short that the nuclear wave packet does not even survive long enough to give a reflected wave; there is then no interference pattern, and the cross sections do not oscillate as a function of energy. This case may be labeled[19] "impulse model," because the nuclear wave packet acquires momentum from the electric field of the extra electron, but does not move appreciably during its residence (unlike the nuclei in the e-N_2 resonance).

The boomerang picture has been used to give qualitative interpretations of experiments and calculations on $e + CO_2$,[32] $e + NO$,[33] and[34] on resonances in $e + N_2$ above 2 eV. A classification of observed resonances on the basis of the boomerang picture was made by Schulz[1] in his review in 1976.

During the last two years, several groups have published calculations related to the boomerang model, either by the method of Ref. 9, or by related methods, on $e + CO$,[35] $e + CO_2$,[36] and $e + N_2$.[37]

D. Born-Oppenheimer approximation

Basic to the boomerang model[9,19,27] is the assumption that the electrons follow the nuclei adiabatically in the quasistationary electronic state $\psi(q, \vec{R})$. We make the assumption only in cases where ψ occupies a volume which is not appreciably larger than the molecule, for example if ψ contains the extra electron in a valence orbital, and is otherwise identical with the ground state of the target (except for a small relaxation due to polarization). We exclude from consideration cases where the electron interacts with the target molecule over distances appreciably larger than molecular dimensions, as for example in the dipole tail from a polar molecule. In such cases the question of adiabatic following becomes very delicate, because even a small angular velocity of the nuclear framework can lead to a large linear velocity of the fluctuations of the dipole potential at a large distance. The point has been discussed by Chang and Fano[38] in their "frame-transformation" approach. An important difference between the Chang-Fano viewpoint and our own is that Chang and Fano regard the nuclei as fixed when the extra electron is within the molecule; by contrast, as we have already emphasized, we regard the relaxation of the nuclei in the electric field of the extra electron as an essential feature when the trapping time is comparable to a vibrational period, or larger.

The adiabatic picture implies that ψ should appear in a product $\psi(q,\vec{R})\xi(\vec{R})$, where ξ is the wave function of the nuclei associated with the trapped electronic state, and that the variation of ψ with respect to $\vec{R}$ should be very slow compared with the variation of ξ.

It has often been suggested that there might be a conflict between the demand for a ψ varying slowly with $\vec{R}$ and the fact that when an electron is scattered at a narrow resonance, a calculation with *fixed* nuclei leads to a jump of π in a resonance phase shift in a range of $\vec{R}$ which becomes small as the width does. However, there is no conflict because the complete wave function in a fixed-nucleus model contains ψ in the form[29] $\psi(q,\vec{R})/[E-W(\vec{R})]$, where $W(\vec{R})$ is the complex resonance energy and E the total energy. The rapid variation of the phase shift at a resonance in a theory without nuclear relaxation comes not from $\psi(q,\vec{R})$, but from the denominator $E-W$, when $\mathrm{Re}\,W \cong E$. When the nuclei are allowed to relax, the rapidly varying factor $[E-W(\vec{R})]^{-1}$ is replaced by the nuclear wave function ξ in a transitory negative ion; in an adiabatic picture, ξ is expected to vary rapidly with $\vec{R}$, so that there is no conflict.

The debate about the Born-Oppenheimer approximation in resonant electron-molecule scattering has been reviewed by Schneider.[39]

E. *Ab initio* calculations and adjustable parameters

No *ab initio* calculation has succeeded in reproducing the observed cross sections, including the vibrational structure, near the 2-eV resonance in $e+N_2$. The most recent *ab initio* calculations for fixed-nucleus models, made by McKoy[40] and Burke[41] and their collaborators, yield a resonance 1 or 2 eV away from the observed position. (There is, of course, no vibrational structure in a fixed-nucleus calculation.)

Improvements have so far been obtained only by the introduction of adjustable parameters; for example,[23] Burke, Chandra, and Buckley can move the resonance in their fixed-nucleus model to the right energy, with a single adjustable parameter.

The most serious attempt at an *ab initio* calculation which allowed for nuclear relaxation is the work[26] of Chandra and Temkin. They find that with a single adjustable parameter, the resonance can be made to appear at the right energy; however, the vibrational structure bears only a superficial resemblance to the experiment, the number of peaks and their spacings both disagreeing with the observations.

Both the magnitude and the vibrational substructure of the cross sections are reproduced by the boomerang calculations (see Ref. 9 and this paper) with the help of six adjustable parameters. One needs that many to describe the potential-energy curve of the intermediate N_2^- ion, and its width (the details are explained in Sec. IV). It is worth emphasizing that in Ref. 9, the six parameters account for all the details of about 50 observed peaks in different excitation channels in the relative cross sections.

Why is it so difficult to reproduce the observed vibrational structure in an *ab initio* calculation? The trouble is probably due to the extreme accuracy demanded by the rapid oscillations in the nuclear wave functions. At a nuclear kinetic energy of 0.5 eV, which is typical of the e-N_2 problem, the reduced nuclear wavelength ($\equiv \lambda\!\!\!^{-}_N$) is $\lambda\!\!\!^{-}_N = 6\times10^{-2}a_0$ ($a_0 = 0.52\times10^{-8}$ cm). Since one must expect to have to locate the nodes and antinodes to better than $\lambda\!\!\!^{-}_N$ to get the maxima and minima of the cross sections at the right energies, one must locate the potential curves of N_2 and N_2^- correctly to about $10^{-2}a_0$. That is a very severe demand on an *ab initio* calculation.

It is our opinion that at present the only practicable method of dealing with the short nuclear wavelength is to use a parametrized potential-energy curve for the transitory N_2^- ion. Such calculations can be brought close to being *ab initio* if one compares the potential-energy curve that fits the experiments with a potential-energy curve calculated *ab initio*. Agreement is satisfactory if the differences are no larger than one expects from the limited accuracy of the calculated curve. This program has been carried through completely in the single example of the $e + N_2$ resonance at 2 eV, where an (almost) *ab initio* curve was calculated by Krauss and Mies.[10] But even they needed to introduce a single adjustable parameter, the correlation energy, to get the resonance appearing at the right energy.

F. Advances beyond earlier calculations

Some development to the theory was needed to make the present calculation possible:

(i) The superelastic cross sections are related to inelastic cross sections by the principle of detailed balancing. We have proved (in Sec. II H) that our approximate theory satisifies this principle.

(ii) To calculate cross sections in absolute magnitude, we have developed a relation between the lifetime (or width) of the compound state and the amplitudes for the entry and exit of the bombarding electron (see Sec. II D). This relation gives one the absolute magnitudes as soon as one has fitted the energy dependence of the relative cross sections; no new parameters must be introduced to make the cross sections absolute.

(iii) The amplitude for vibrationally elastic scattering contains a direct component in addition to the resonant component which dominates the inelastic scattering. We have incorporated the direct amplitudes into the theory.

(iv) The previous theory[9] was formulated without exchange of the projectile and target electrons. We have now incorporated exchange, in Sec. II G.

We have also taken this opportunity to give a simpler derivation of the theory than that in Ref. 9, and to clarify a number of minor points.

G. Plan of this paper

The theory is developed in Sec. III. Calculated results are presented and compared with experiment in Sec. III. The results are discussed in Sec. IV.

II. THEORY

A. Initial and final states

Consider the scattering of an electron from an initial state $\exp(i\vec{k}_i \cdot \vec{r})\alpha_i$ to a final state $\exp(i\vec{k}_f \cdot \vec{r})\alpha_f$ by a molecule whose initial and final states are $\phi_i(q, \vec{R})\chi_i(\vec{R})$ and $\phi_f(q, \vec{R})\chi_f(\vec{R})$. Here $\hbar\vec{k}_i$ and $\hbar\vec{k}_f$ are the initial and final momenta, α_i and α_f are the initial and final spin states of the projectile, χ_i and χ_f are the initial and final vibrational states, and ϕ_i and ϕ_f are the initial and final electronic states of the molecule. The functions ϕ_i and ϕ_f are antisymmetric with respect to exchange of the target electrons; we shall adopt the convention that they are to be written $\phi_i(1, 2, \ldots, N)$ and $\phi_f(1, 2, \ldots, N)$, with the target electrons appearing in ascending order from left to right. The position of the nuclei is denoted collectively by $\vec{R}$. The symbol q is to stand for the totality of electronic coordinates; wherever we have to single out the spatial coordinate of the arriving or departing electron, we shall denote it by $\vec{r}$.

The complete initial and final states are

$$\Phi_i = \exp(i\vec{k}_i \cdot \vec{r})\phi_i\alpha_i\chi_i$$

and

$$\Phi_f = \exp(i\vec{k}_f \cdot \vec{r})\phi_f\alpha_f\chi_f .$$

We shall initially ignore the exchange of the projectile with the target electrons, and return to discuss exchange in Sec. II G. We shall regard the direction of the molecular axis as fixed; this approximation should be good as long as the lifetime of the electronic state is short compared with a rotational period; in the e-N_2 resonance at ~2 eV, the lifetime is at most of the order of a vibrational period, about 10^{-14} Sec., while the rotational period at room temperature is about 100 times as long, of the order of 10^{-12} sec. We continue to restrict ourselves to a diatomic molecule; its axis lies in the direction $\hat{R}$.

The Hamiltonian is

$$H = H_e(q, \vec{R}) + K, \tag{2.1}$$

where H_e is the electronic Hamiltonian corresponding to nuclei at $\vec{R}$, and K is the kinetic energy of the nuclear vibration along $\hat{R}$. The mass center will be regarded as fixed. The Schrödinger equation at energy E is

$$(H - E)\Psi_i = 0, \tag{2.2}$$

where Ψ_i is the complete state; it has the form $\Psi_i = \Phi_i +$ (scattered waves).

B. Electronic compound state and adiabatic criterion

In the e-N_2 resonance at 2 eV, the scattering involves two electronic resonant states ψ_+ and ψ_-, each of which consists of an N_2 molecule in its electronic ground state, with an additional electron in a π_g orbital; this happens to be the lowest vacant orbital in the N_2 molecule. In an expansion of the π_g orbital in spherical harmonics, the lowest l value is $l = 2$; this angular momentum provides the centrifugal potential barrier which traps the extra electron. There is one unit of orbital angular momentum about the axis; the subscript + or - distinguishes between the two directions. The states ψ_+ and ψ_- are eigenfunctions of H_e:

$$[H_e(q,\vec{R}) - W(\vec{R})]\,\psi_\pm(q,\vec{R}) = 0\,, \qquad (2.3)$$

where $W(\vec{R})$ is the eigenvalue at the nuclear configuration $\vec{R}$. We shall see that $W(\vec{R})$ becomes the energy surface of the negative ion.

The functions $\psi_\pm$ cannot be normalized by integrating $|\psi_\pm|^2$ over all space because autoionization gives them tails of outgoing waves, which would make the integral $\int dq\,|\psi_\pm|^2$ diverge if it were taken over all space. Therefore we introduce a finite volume, called the "interior region" or IR, which encloses the target molecule. The boundaries of the IR will be discussed later. We shall normalize ψ so that $\int_{\mathrm{IR}} dq\,|\psi_\pm|^2 = 1$, where the subscript IR means that the integration is to be restricted to the IR.

At the boundary of the IR, the exact wave function matches onto outgoing waves corresponding to the vibrational and rotational states which can be excited in the molecular target, in addition to the incident plane wave. To define $\psi_\pm$ as solutions of (2.3), we shall use an adiabatic approximation, by matching $\psi_\pm$ onto outgoing waves at the boundary of the internal region as if the escaping electron came from a molecule with stationary nuclei. The justification comes from the Franck-Condon principle, which states that the emission of an electron must occur without change of momentum by the nuclei; therefore the kinetic energies of the nuclei before and after emission must be equal. If E is the total energy, ϵ_f the energy of the final molecule, $W(\vec{R})$ the potential-energy surface in the negative ion, and $V_f(\vec{R})$ the potential-energy surface of the final molecule, then $E - W(\vec{R}) = \epsilon_f - V_f(\vec{R})$. Therefore $E - \epsilon_f = W(\vec{R}) - V_f(\vec{R})$, and since the emerging electron carries away kinetic energy $E - \epsilon_f$, the configuration $\vec{R}$ emits electrons of energy $W(\vec{R}) - V_f(\vec{R})$. This is completely determined by $\vec{R}$, just as if the nuclei were stationary. Of course this result is only approximately true, because the Franck-Condon principle is itself only approximately true.

In matching $\psi_\pm$ on to outgoing waves, at the bound boundary of the IR, we shall take the energy of the outgoing wave to be the eigenvalue $W(\vec{R})$ which appears in (2.3). This specification of the resonant state was originally proposed by Siegert[42]; it is closely related to an earlier formulation by Kapur and Peierls,[29] who used the energy of the scattering experiment, and the even earlier formulation by Gamow.[28] One advantage of Siegert's prescription is that it is straightforward to show that the eigenvalue W is independent of just where one cuts off the internal region; by contrast, the Kapur-Peierls formulation gives one eigenvalues which depend somewhat on where the IR is cut off. It is straightforward to show that Siegert's prescription makes the eigenvalues $W(\vec{R})$ complex, if the real part is sufficiently high to permit autoionization; we shall follow convention by writing

$$W(\vec{R}) = \mathrm{Re}\,W(\vec{R}) - \tfrac{1}{2}\Gamma(\mathrm{R}),$$

where Γ is real, and >0.

The boundary of the IR is conveniently chosen so that $\psi_\pm$ falls in amplitude with increasing radius within the boundary, and joins onto an oscillating outgoing wave outside. Since the confinement of the e-N_2 resonance at ~2 eV is due to a barrier from the centrifugal potential, we choose the boundary of the IR to be the outer limit a of the centrifugal barrier, given by $ka = [l(l+1)]^{1/2}$. Here k is the average wave number of the escaping electrons, and l the orbital angular momentum in the dominant component of the wave function of the extra electron in an expansion in spherical harmonics outside the molecular core; for the e-N_2 resonance at ~2 eV, one has $l = 2$. At 2.3 eV, one has $k \approx 0.41\,a_0^{-1}$ (where $a_0 = 0.52\times10^{-8}$ cm); one finds $a = 6.0a_0$ for the radius at the boundary of the IR.

C. Nuclear wave equation

We need the complete state Ψ_i only within the region where the extra electron interacts strongly with the target molecule, because the differential scattering cross section is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{i\to f} = \left(-\frac{m}{2\pi\hbar^2}\right)^2 \frac{v_f}{v_i}\,|(\Phi_f|\,V\,|\Psi_i)|^2\,, \qquad (2.4)$$

where Φ_i and Φ_f are the initial and final states mentioned in Sec. II A, V is the interaction of the extra electron with the molecule, and v_f and v_i are the velocities of the scattered and incident electrons.

Within the internal region we write

$$\Psi_i(q,\vec{R};\vec{k}_i) = \Phi_i(q,\vec{R};\vec{k}_i) + \psi_+(q,\vec{R})\,\xi_+(\vec{R},\vec{k}_i) + \psi_-(q,\vec{R})\,\xi_-(\vec{R},\vec{k}_i) + \Delta\Psi_i\,, \qquad (2.5)$$

where ξ_+ and ξ_- remain to be determined. The function $\Delta\Psi_i$ is to contain all the distortion of the wave function associated with direct scattering, that is all the distortion in Ψ_i which cannot be represented by ψ_+ and ψ_-. We shall suppose that direct scattering is negligible for the symmetry of ψ_+ and ψ_- in a frame fixed in the molecule. However, direct scattering with $l = 0$ and $l = 1$ will be taken into account.

To determine ξ_+ and ξ_-, insert (2.5) into (2.2), multiply in turn by ψ_+^* and ψ_-^*, and integrate over the electron coordinates within the internal region. Two approximations will be made:

(i) Take

$$\int_{\mathrm{IR}} dq\ \psi_{\pm}^{*}(H_e - E)\Delta\Psi_i = 0, \tag{2.6}$$

because of our assumption that there is no direct scattering with the same symmetry as ψ_+ and ψ_- in the molecular frame.

(ii) Make the adiabatic approximation

$$K[\psi_+\xi_+] \to \psi_+ K\xi_+, \quad K[\psi_-\xi_-] \to \psi_- K\xi_-, \tag{2.7}$$

because ψ_+ and ψ_- are expected to vary slowly with $\vec{R}$ in comparison with ξ_+ and ξ_-. [As in (2.1), K is the nuclear vibrational kinetic energy.] The terms neglected in (2.7) contain derivatives of $\psi_\pm$ with respect to $\vec{R}$. They are of order $(p_e p_N/M)\psi\xi$, where p_e is an electronic momentum, p_N a nuclear momentum, and M a nuclear mass. The approximation is justified if these neglected terms are small compared with the other terms in the Schrödinger equation, that is the Coulomb interactions, the electronic kinetic energy, and the nuclear kinetic energy. The electronic kinetic energy and the Coulomb interactions are of the same order, because of the virial theorem; they are of the order of 1 a.u. The nuclear kinetic energy is much smaller, of the order of $(m/M)^{1/2} \approx 0.01$ a.u. in a low vibrational state of the neutral (where m is the electronic mass). Thus the neglect of the terms $p_e p_N/M$ will be justified if they are much smaller than the nuclear kinetic energy $\frac{1}{2}p_N^2/M$, in other words if $p_e/p_N \ll 1$. In a low vibrational state of the neutral, one has $p_e/p_N \approx (m/M)^{1/4} \approx 0.1$; in the e-N_2 shape resonance, p_e is of the same order, since valence orbitals are involved, but p_N may be somewhat larger because the molecule becomes vibrationally excited. Therefore the ratio p_e/p_N should be somewhat smaller than 0.1, so that the approximation (2.7) should be well satisfied.

Split up the Hamiltonian

$$H = H_e + K = H_0 + V, \tag{2.8}$$

where $(H_0 - E)\Phi_i = 0$. Then

$$\int_{\mathrm{IR}} dq\ \psi_{\pm}^{*}(H - E)\Phi_i = \int_{\mathrm{IR}} dq\ \psi_{\pm}^{*} V \Phi_i. \tag{2.9}$$

With the aid of (2.6)–(2.9), one finds from (2.2)

$$[K + W(\vec{R}) - E]\xi_\pm(\vec{R}) = -\zeta_{i\pm}'(\vec{R}, \vec{k}_i)\chi_i(\vec{R}), \tag{2.10}$$

where

$$\zeta_{i\pm}'(\vec{R}, \vec{k}_i) \equiv \int_{\mathrm{IR}} dq\ \psi_{\pm}^{*} V e^{i\vec{k}_i \cdot \vec{r}} \phi_i \alpha_i. \tag{2.11}$$

Equation (2.10) is the wave equation for the nuclear wave function $\xi_\pm$ in the negative ion. The integral $\zeta_{i\pm}'(\vec{R}, \vec{k}_i)$ will be called the "electron entry amplitude." Since we are regarding the orientation of the molecule as fixed, there is no rotational kinetic energy in K.

Cross sections can be calculated from (2.4) and (2.5) as soon as ξ_+ and ξ_- have been determined from (2.10). For the scattering from the incident state Φ_i to the final state Φ_f, one finds

$$\left(\frac{d\sigma}{d\Omega}\right)_{i\to f} = \frac{v_f}{v_i}|T_{i\to f}|^2, \tag{2.12}$$

where

$$T_{i\to f} = T_{i\to f}^{\mathrm{pot}} + T_{i\to f}^{\mathrm{res}}, \tag{2.13}$$

with

$$T_{i\to f}^{\mathrm{pot}} = -\frac{m}{2\pi\hbar^2}[\Phi_f | V | (\Phi_i + \Delta\Psi_i)], \tag{2.14a}$$

$$T_{i\to f}^{\mathrm{res}} = -\frac{m}{2\pi\hbar^2}[(\chi_f | \zeta_{f+}(\vec{R}, \vec{k}_f) | \xi_+) + (\chi_f | \zeta_{f-}(\vec{R}, \vec{k}_f) | \xi_-)], \tag{2.14b}$$

$$\zeta_{f\pm}(\vec{R}, \vec{k}_f) \equiv \int_{\mathrm{IR}} dq (e^{i\vec{k}_f \cdot \vec{r}} \phi_f \alpha_f)^* V \psi_\pm. \tag{2.14c}$$

The integral (2.14c) may be called the "electron exit amplitude." It follows from (2.11) and (2.14c) that

$$\zeta_{f\pm}'(\vec{R}, \vec{k}) = \zeta_{f\pm}(\vec{R}, \vec{k})^*. \tag{2.15}$$

D. Entry and exit amplitudes

To calculate cross sections in absolute magnitude, one needs the entry and exit amplitudes in (2.11) and (2.15). We next show that the $\zeta_{i\pm}$ and $\zeta_{i\pm}'$ can be expressed in terms of Γ if there is only a single electronic channel open. This is usually the case in a shape resonance, and happens to be true for the e-N_2 resonance at ~2 eV; on autoionization, the extra electron vacates its orbital and leaves the molecule in its electronic parent state. The significance of the relation between $\zeta_{i\pm}$, $\zeta_{i\pm}'$, and Γ is that one can often determine Γ by fitting the energy dependence and relative magnitudes of cross sections, but without regard to the absolute magnitudes. The link between Γ and $\zeta_{i\pm}$ and $\zeta_{i\pm}'$ then enables one to assign absolute magnitudes to the cross sections without further adjustment of parameters.

Consider the fictitious problem in which the nuclei are fixed. We shall distinguish quantities belonging to the fixed-nucleus problem by a superscript F; for example the initial and final states are Φ_i^F and Φ_f^F. The Hamiltonian is now $H^F = H_e$, the nuclear kinetic energy K being dropped. In place of (2.5), we have

$$\Psi_i^F = \Phi_i^F + \psi_+\xi_+^F + \psi_-\xi_-^F + \Delta\Psi_i^F,$$

where the electronic resonant functions ψ_+ and ψ_- are the same as before, because they were always defined relative to fixed nuclei. The equation for ξ_+^F and ξ_-^F becomes, in place of (2.10),

$$[W(\vec{R})-E]\xi_\pm^F=-\zeta'_{i\pm}(\vec{R},\vec{k}_i),$$

where $\zeta'_{i\pm}$ is still given by (2.11); $\vec{k}_i$ is the wave vector of the incoming electron.

We shall suppose that only a single electronic state is energetically accessible, so that the initial and final electronic states of the molecule are identical; therefore we can drop the suffices i and f from ζ_i and ζ'_f, and write $\zeta'_\pm$ in place of $\zeta'_{i\pm}$, and $\zeta_\pm$ in place of $\zeta_{f\pm}$.

In place of (2.13), one has

$$T^F_{i\to f}=T^{\text{pot}\,F}_{i\to f}+T^{\text{res}\,F}_{i\to f}, \tag{2.16a}$$

$$T^{\text{pot}\,F}_{i\to f}=-\frac{m}{2\pi\hbar^2}\left(\Phi_f^F\middle|V\middle|\Phi_i^F+\Delta\Psi_i^F\right), \tag{2.16b}$$

$$T^{\text{res}\,F}_{i\to f}$$
$$=-\frac{m}{2\pi\hbar^2}\,\frac{\zeta_+(\vec{R},\vec{k}_f)\zeta'_+(\vec{R},\vec{k}_i)+\zeta_-(\vec{R},\vec{k}_f)\zeta'_-(\vec{R},\vec{k}_i)}{E-W(\vec{R})}, \tag{2.16c}$$

where $\vec{k}_f$ is the wave number of the outgoing electron. In place of (2.12),

$$\left(\frac{d\sigma^F}{d\Omega}\right)_{i\to f}=|T^F_{i\to f}|^2, \tag{2.17}$$

since the initial and final velocities are now equal.

According to the optical theorem, the total cross section σ_T^F, corresponding to fixed nuclei, is given by

$$\sigma_T^F=(4\pi/k_i)\,\mathrm{Im}\,T^F_{ii}. \tag{2.18}$$

This expression consists of terms which behave, near the resonance at $E=W(\vec{R})$, like $(E-W)^{-2}$, $(E-W)^{-1}$, and a constant. The coefficient of $(E-W)^{-2}$ becomes

$$\frac{4\pi}{k_i}[\tfrac{1}{2}\Gamma(\vec{R})]\frac{m}{2\pi\hbar^2}\mathrm{Re}[\zeta_+(\vec{R},\vec{k}_i)\zeta'_+(\vec{R},\vec{k}_i)$$
$$+\zeta_-(\vec{R},\vec{k}_i)\zeta'_-(\vec{R},\vec{k}_i)]. \tag{2.19}$$

One may average (2.19) over the orientation of the molecule, because the orientation may be supposed to be random. However, it is easier to average over the direction $\hat{k}_i$ of the incident beam instead. This average is the same for the two terms in (2.19), because the states ψ_+ and ψ_- differ only by a reflection in a plane passing through the molecular axis. The coefficient of $|E-W|^{-2}$ in (2.18) becomes, with the aid of (2.15),

$$\frac{\Gamma(\vec{R})}{k_i}\,\frac{m}{2\pi\hbar^2}\int d\hat{k}_i\,|\zeta'_+(\vec{R},\vec{k}_i)|^2; \tag{2.20}$$

we could have written ζ'_- in place of ζ'_+.

Another expression for the total cross section comes from integrating (2.12) over all final directions. We may set $v_f=v_i$, because the nuclei have been supposed to be fixed, and at ~2 eV no excited electronic states of the N_2 molecule are accessible. In the integral over all directions $\hat{k}_f$, there is no interference between the two terms in the numerator of $E-W(\vec{R})$ in (2.16c), because the outgoing waves belong to opposite angular momenta about the molecular axis. With the aid of (2.15), one finds from (2.17) and (2.16c)

$$\sigma_T^F=\int|T^F_{i\to f}|^2d\hat{k}_f$$
$$=\frac{1}{4\pi}\left(\frac{m}{2\pi\hbar^2}\right)^2\frac{1}{|E-W|^2}\left(\int d\hat{k}_f\,|\zeta_+(\vec{R},\vec{k}_f)|^2\int d\hat{k}_i\,|\zeta'_+(\vec{R},\vec{k}_i)|^2+\int d\hat{k}_f\,|\zeta_-(\vec{R},\vec{k}_f)|^2\int d\hat{k}_i\,|\zeta'_-(\vec{R},\vec{k}_i)|^2\right) \tag{2.21}$$
$$+[\text{terms of order }(E-W)^{-1}];$$

we have again written $\zeta_\pm$ and $\zeta'_\pm$ without subscripts denoting initial and final electronic states, because only the elastic electronic channel is accessible energetically. The cross section (2.21) is an average over the direction $\hat{k}_i$, which is equivalent to an average over the directions of the molecular axis with $\hat{k}_i$ held fixed. From (2.15), and the fact that the integrals containing ζ'_+ and ζ'_- are equal (since the functions ψ_+ and ψ_- differ only by a reflection in a plane containing the molecular axis), the coefficient of $|E-W|^{-2}$ in (2.21) becomes

$$\frac{1}{2\pi}\left(\frac{m}{2\pi\hbar^2}\right)^2\left(\int d\hat{k}_i\,|\zeta'_+(\vec{R},\vec{k}_i)|^2\right)^2. \tag{2.22}$$

By equating (2.20) and (2.22), one finds

$$\frac{1}{4\pi}\int d\hat{k}\,|\zeta'_\pm(\vec{R},\vec{k}_i)|^2=\frac{\pi\hbar^2}{mk_i}\Gamma(\vec{R}). \tag{2.23}$$

$|k_i|$ should be taken at the center of the resonance, since we have worked with the terms $|E-W|^{-2}$ in deriving (2.23). Equation (2.23) is the sought-for relation between Γ and $|\zeta'_\pm|$.

E. Separation of angular dependence

For our diatomic molecule, it is convenient to decompose $\zeta_\pm$ and $\zeta'_\pm$ into factors which describe the angular distribution of the incoming and outgoing electron, and the variation of the tunneling amplitude with the separation of the nuclei. We write

$$\zeta'_\pm(\vec{R},\vec{k}) = \tilde{\zeta}(R,k)A_\pm(\vec{R},\vec{k}), \tag{2.24}$$

where

$$\tilde{\zeta}(R,k) = \left(\int d\hat{k}\,|\zeta'_\pm(\vec{R},\vec{k})|^2\right)^{1/2}, \tag{2.24a}$$

$$A_\pm(\vec{R},\vec{k}) \equiv \zeta'_\pm(\vec{R},\vec{k})/\tilde{\zeta}(R,k), \tag{2.24b}$$

and

$$\int d\hat{k}\,|A_\pm(\vec{R},\vec{k})|^2 = 1. \tag{2.24c}$$

We shall choose the positive root in (2.24a). There is no suffix on $\tilde{\zeta}(R,k)$ because ψ_+ and ψ_- are mirror images with respect to a plane containing the molecular axis. The independence of $\tilde{\zeta}(R,k)$ from the directions of $\vec{R}$ and $\vec{k}$ follows from definition (2.24a). It follows from (2.23), (2.24), (2.24b), and (2.24c) that

$$\tilde{\zeta}(R,k) = [(4\pi^2\hbar^2/mk)\Gamma(R)]^{1/2}. \tag{2.25}$$

A valuable approximation for $\tilde{\zeta}$ comes from (2.11), if one expands

$$\exp(i\vec{k}_i\cdot\vec{r}) = 4\pi\sum_{lm} i^l j_l(k_i r)\mathcal{Y}^*_{lm}(\hat{k}_i)\mathcal{Y}_{lm}(\hat{r}),$$

and notes that

$$j_l(kr) \cong (kr)^l/(2l+1)!!$$

if

$$kr \lesssim l,$$

where

$$(2l+1)!! = 1\times3\times5\times\ldots\times(2l+1).$$

[For example, for $l=2$, one has $j_2(1.0)=0.062$, $j_2(2.0)=0.20$, while the approximate values are $1.0^2/5!!=0.067$, $2.0^2/5!!=0.27$.] Since the resonant orbitals $\psi_\pm$ have large values only well within the internal region in (2.11), the approximation for $j_2(k_i r)$ will be justified in the integral. Moreover, the higher terms in the expansion of $\exp(i\vec{k}\cdot\vec{r})$ are sufficiently small to be neglected; for example at the boundary of the internal region,

$$j_4(2.0)/j_2(2.0) = 0.09.$$

If one retains only the lowest term in the expansion of $\exp(i\vec{k}_i\cdot\vec{r})$ which gives a nonzero contribution to $\zeta_{i\pm}$ in Eq. (2.11), the factor A in (2.24) becomes

$$A_\pm(\vec{R},\vec{k}) \to \mathcal{Y}^*_{l(\min)m(\pm)}(\hat{R},\hat{k}); \tag{2.26a}$$

$l(\min)$ is the lowest l which gives a nonzero contribution; $m(\pm)$ is the value of m which corresponds to the subscript ± on A. The appearance of $\hat{R}$ in the argument on the right signifies that the molecular axis is to be used as the polar axis for the angles in $\hat{k}$. From (2.24a), it follows that

$$\tilde{\zeta}(R,k) = \tilde{\zeta}^*(R,k) \tag{2.26b}$$

in (2.24).

The dependence of Γ and $\tilde{\zeta}$ on the energy of the emitted or absorbed electron becomes explicit if one replaces $\exp(i\vec{k}_i\cdot\vec{r})$ in (2.11) by the lowest contributing term in the spherical harmonic expansion. If one further approximates

$$j_l(kr) \cong (kr)^l/(2l+1)!!$$

in (2.11), one finds $\zeta_{i\pm}\propto k^{l(\min)}$, where $l(\min)$ is the lowest contributing value of l in the expansion for $\exp(i\vec{k}_i\cdot\vec{r})$. Therefore, according to (2.23),

$$\Gamma(\vec{R}) \propto k(\vec{R})^{2l(\min)+1}, \tag{2.27}$$

where $k(R)$ is the wave number of an electron absorbed or emitted by the fictitious molecule with its nuclei fixed at $\vec{R}$.

Following Blatt and Weisskopf[43] and taking $l(\min) = 2$ for the $^2\Pi_g$ resonance in N_2, we shall use the more accurate expression

$$\Gamma(\vec{R}) = \Gamma(\vec{R}_0)\frac{k(\vec{R})}{k(\vec{R}_0)}\frac{v_2[k(\vec{R})\rho]}{v_2[k(\vec{R}_0)\rho]}, \tag{2.28a}$$

where

$$v_2(\chi) \equiv \chi^4/(9+3\chi^2+\chi^4): \tag{2.28b}$$

There $\vec{R}_0$ is the equilibrium separation of the nuclei; ρ is an estimate of the distance from the mass center beyond which the centrifugal potential of the projectile electron dominates over its Coulomb and polarization interactions with the molecule.

In using (2.28), we are supposing that the variation of ψ_+, V, and ϕ with $\vec{R}$ in (2.11) is sufficiently slow to leave the factor kv_2 dominant.

With relations (2.23) and (2.25) established from the fictitious model with fixed nuclei, we now return to the problem of vibrating nuclei.

F. Calculation of resonant scattering amplitude

To calculate cross sections from (2.12), one must find $\xi_\pm$ in (2.5) by solving (2.10). We shall suppose that only a single electronic state is accessible energetically, so that the subscript i may be dropped from $\zeta_{i\pm}$ in (2.10); however, we shall retain the suffices i and f on χ_i and χ_f to distinguish the different vibrational states.

Substitute (2.24) and (2.26a) into (2.10), and drop a factor $\mathcal{Y}^*_{l(\mathrm{min}),m(\pm)}$ by writing

$$\xi_\pm(\vec{R},\vec{k}_i)=(\tilde{\xi}/R)(R,k_i)\mathcal{Y}^*_{l(\mathrm{min})m(\pm)}(\hat{R},\hat{k}_i). \qquad (2.29)$$

$\tilde{\xi}(R,k_i)$ now depends only on the magnitudes, but not the directions of $\vec{R}$ and $\vec{k}_i$. One finds

$$[\tilde{K}(R)+W(R)-E]\tilde{\xi}(R,k_i)=-\tilde{\zeta}(R,k_i)\tilde{\chi}_i(R), \qquad (2.30)$$

where

$$\tilde{\chi}_i(R)\equiv R\chi_i,\quad \tilde{K}(R)\equiv-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial R^2}, \qquad (2.31)$$

M being the reduced mass.

The resonant part $T^{\mathrm{res}}_{i\to f}$ in (2.13) becomes, with the aid of (2.14b) (2.15), (2.26a), and (2.26b),

$$T^{\mathrm{res}}_{i\to f}= -(m/2\pi\hbar^2)[\mathcal{Y}_{l(\mathrm{min})m(+)}(\hat{R},\hat{k}_f)\mathcal{Y}^*_{l(\mathrm{min})m(+)}(\hat{R},\hat{k}_i)+\mathcal{Y}_{l(\mathrm{min})m(-)}(\hat{R},\hat{k}_f)\mathcal{Y}^*_{l(\mathrm{min})m(-)}(\hat{R},\hat{k}_i)] \cdot(\chi_f|\tilde{\zeta}(R,k_f)|(\tilde{\xi}/R)(R,k_i)) \qquad (2.32)$$

G. Exchange

So far, we have singled out one electron as the projectile and scattered particle, and ignored the possibility that this one electron may be exchanged for one of the target electrons. This restriction will now be removed.

Suppose that the target molecule contains N electrons, so that there are $N+1$ electrons altogether. In place of the state Φ_i in Sec. II A, we introduce $N+1$ states Φ_{ip}, where the suffix p $[=1,2\ldots,(N+1)]$ stands for the incident electron:

$$\Phi_{ip}[1,2\ldots,(N+1)]\equiv(-1)^p\exp(i\vec{k}_i\cdot\vec{r}_p)\phi_i[1,2,\ldots,(p-1),(p+1),\ldots,(N+1)]\alpha_i(p)\chi_i(\vec{R}). \qquad (2.33)$$

The factor $(-1)^p$, together with the antisymmetry of Φ_i and the order in which the coordinates in ϕ_i are written (see Sec. II A) ensure that

$$P_{qp}\Phi_{ip}[1,2,\ldots,(N+1)]=-\Phi_{iq}, \qquad (2.34)$$

where P_{qp} is the operator which interchanges the coordinates of p and q.

We shall denote by $\Psi_{ip}[1,2,\ldots,(N+1)]$ that solution of the Schrödinger equation

$$(H-E)\Psi_{ip}=0 \qquad (2.35)$$

which behaves like

$$\Psi_{ip}\to\Phi_{ip}+(\text{outgoing waves}) \qquad (2.36)$$

when any one electron moves off to infinity. Since any of the $N+1$ electrons can be the projectile, the physical solution of the Schrödinger equation, which we denote by Ψ^{ex}_i, is

$$\Psi^{\mathrm{ex}}_i=(N+1)^{-1/2}\sum_{p=1}^{N+1}\Psi_{ip}. \qquad (2.37)$$

It follows from (2.34) and the antisymmetry of ϕ_i that Ψ^{ex}_i antisymmetric in all $N+1$ electrons; we have attached the superscript "ex" to remind us of this. The factor $(N+1)^{-1/2}$ makes the incoming flux for Ψ^{ex}_i the same as for the no-exchange function Ψ_i in Eq. (2.2).

The amplitude for the emission of electron spin-spin state α_f, with momentum $\vec{k}_f$, leaving the molecule in state ϕ_f is

$$T_{i\to f\ s}=-(m/2\pi\hbar^2)(\Phi_{fs}|V_s|\Psi^{\mathrm{ex}}_i), \qquad (2.38)$$

where V_s is the interaction potential between electron s and all the other particles. It follows from (2.34) and the antisymmetry of Ψ^{ex}_i that $T_{i\to f\ s}$ is the same for all s.

The observed outgoing flux is the sum of the outgoing fluxes for the $N+1$ electrons, so that the differential scattering cross section with exchange per unit solid angle in direction $\hat{k}_f$ and into spin state α_f is

$$\left(\frac{d\sigma^{\mathrm{ex}}}{d\Omega}\right)_{i\to f}=(N+1)\frac{v_f}{v_i}|T_{i\to f\ s}|^2,$$

where s stands for any one of the $N+1$ electrons and v_i and v_f are the initial and final velocities. We can absorb the factor $N+1$ by defining $\sqrt{N+1}\,T_{i\to f\ s}\equiv T^{\mathrm{ex}}_{i\to f}$. Then, from (2.37) and (2.38),

$$T^{\mathrm{ex}}_{i\to f}=-\frac{m}{2\pi\hbar^2}\sum_{p=1}^{N+1}(\Phi_{fs}|V_s|\Psi_{ip}), \qquad (2.39)$$

$$\left(\frac{d\sigma^{\mathrm{ex}}}{d\Omega}\right)_{i\to f}=\frac{v_f}{v_i}|T^{\mathrm{ex}}_{i\to f}|^2. \qquad (2.40)$$

Expression (2.39) is the same whichever electron appears as s.

We next separate Ψ_{ip} (from 2.36) into resonant and direct parts. Introduce electronic compound states $\psi_{\pm p}(q, \vec{R})$ in which electron p occupies an orbital above the filled shells of the target molecule:

$$\begin{aligned}&\psi_{\pm p}[1, 2, \ldots, (N+1)]\\ &\quad = (-1)^p \pi_{\pm}(p)\\ &\quad \times \phi_i[1, 2, \ldots, (p-1), (p+1), \ldots, (N+1)];\end{aligned} \tag{2.41}$$

π_+ and π_- are the orbitals occupied by the extra electron; they are orthogonal to the orbitals of the core electrons, and normalized over the internal region. [We shall need the factor $(-1)^p$ in (2.44) below.] Therefore

$$\int_{\mathrm{IR}} dq |\psi_{\pm p}[1, 2, \ldots, (N+1)]|^2 = 1. \tag{2.42}$$

The functions $\psi_{\pm}$ in the no-exchange theory in Sec. II B had the form (2.41), with the chosen projectile in the role of p. With the aid of $\psi_{\pm p}$, we may write out Ψ_{ip} (from 2.36) in the manner of (2.5), with a subscript p on all terms to distinguish the projectile:

$$\Psi_{ip} = \Phi_{ip} + \Delta\Psi_{ip} + \psi_{+p}\xi_+ + \psi_{-p}\xi_-. \tag{2.43}$$

Equation (2.10) follows as before, with

$$\begin{aligned}&\zeta'_{i\pm}(\vec{R}, \vec{k}_i)\\ &\quad \equiv \int_{\mathrm{IR}} dq\ \psi^*_{\pm p} V_p e^{i\vec{k} \cdot \vec{r}_p}\\ &\quad \times \phi_i[1, 2, \ldots, (p-1),\\ &\qquad (p+1), \ldots, (N+1)]\alpha_i(p).\end{aligned} \tag{2.44}$$

This integral is independent of which electron p has been singled out, as one may show from the antisymmetry of ϕ_i and definition (2.41). Therefore the coefficients $\xi_{\pm}$ are independent of p; $\Phi_{ip} + \Delta\Psi_{ip}$ is the direct part of Ψ_{ip}, and $\psi_{+p}\xi_+ + \psi_{-p}\xi$ is the resonant part.

We can now separate the scattering amplitude $T^{\mathrm{ex}}_{i\to p}$ into direct and resonant parts. With (2.43), one has from (2.39)

$$T^{\mathrm{ex}}_{i\to f} = T^{\mathrm{ex,pot}}_{i\to f} + T^{\mathrm{ex,res}}_{i\to f}, \tag{2.45}$$

where

$$T^{\mathrm{ex,pot}}_{i\to f} = -\frac{m}{2\pi\hbar^2}\sum_{p=1}^{N+1} [\Phi_{fs}|V_s|(\Phi_{ip} + \Delta\Psi_{ip})], \tag{2.46}$$

$$T^{\mathrm{ex,res}}_{i\to f} = -\frac{m}{2\pi\hbar^2}\sum_{p=1}^{N+1} [\Phi_{fs}|V_s|(\psi_{+p}\xi_+ + \psi_{-p}\xi_-)]. \tag{2.47a}$$

Since the orbitals $\pi_{\pm}$ in $\psi_{\pm}$ are orthogonal to the others, only the term $p = s$ contributes to (2.47a), so that

$$T^{\mathrm{ex,res}}_{i\to f} = -(m/2\pi\hbar^2)[\Phi_{fs}|V_s|(\psi_{+s}\xi_+ + \psi_{-s}\xi_-)]. \tag{2.47b}$$

This expression has the same value irrespective of which electron appears as s.

The resonant scattering amplitude with exchange, in (2.47b), is identical with (2.14b) and (2.14c) in the theory without exchange in Sec. II C. Therefore resonant scattering remains unchanged when exchange is included. The direct amplitude with exchange [in (2.46)] differs from the expression (2.14a) of the no-exchange theory only by the addition of exchange terms.

H. Detailed balancing

The scattering amplitude (2.32) or (2.47b) may be shown to satisfy a condition of detailed balancing:

$$|T^{\mathrm{res}}_{i\to f}|^2 = |T^{\mathrm{res}}_{f\to i}|^2. \tag{2.48}$$

(The corresponding result for the cross sections is given in Sec. II J.) To prove this result, write

$$\tilde{\xi}(R, k_i) = -\int_0^\infty dR'\, G(R, R'; E)\tilde{\zeta}(R', k_i)\tilde{\chi}_i(R'), \tag{2.49}$$

where G is the Green's function for Eq. (2.30), which satisfies

$$[\tilde{K}(R) + W(R) - E]G(R, R'; E) = \delta(R - R'). \tag{2.50}$$

The last factor in (2.32) becomes (if we recall that the radial factor in the volume element in spherical polar coordinates is $R^2\, dR$)

$$\begin{aligned}&\left(\chi_f \middle| \tilde{\zeta}(R, k_f) \middle| \frac{\tilde{\xi}(R, k_i)}{R}\right)\\ &\qquad = -\int \tilde{\chi}^*_f(R) dR\ \tilde{\zeta}(R, k_f) G(R, R'; E)\\ &\qquad\quad \times \tilde{\zeta}(R', k_i) dR'\ \tilde{\chi}_i(R').\end{aligned} \tag{2.51}$$

Since $\tilde{\chi}_f$ is a bound vibrational state, it may be taken to be real. Therefore the symmetry relation (2.48) would follow if we could show that

$$G(R, R'; E) = G(R', R; E). \tag{2.52}$$

To prove (2.52), note that according to (2.49), $G(R, R'; E)$ has to satisfy the same boundary condition as $\tilde{\xi}$ as a function of R. As $R \to 0$, $\tilde{\xi} \to 0$, because of the factor R^{-1} in the definition (2.29); as $R \to \infty$, either $\tilde{\xi} \to 0$ [if $\mathrm{Re}\, W(\infty) > E$] or $\partial\tilde{\xi}/\partial R - i\kappa\tilde{\xi} \to 0$ [if $\mathrm{Re}\, W(\infty) > E$], where κ is the wave number of the motion of separation. Now multiply (2.50) by $G(R, R''; E)$, (where R'' is arbitrary), integrate over R, and subtract the same equation with R' and R'' interchanged. With the identity

$$G(R,R'')\frac{\partial^2}{\partial R^2}G(R,R')-G(R,R')\frac{\partial^2 G(R,R'')}{\partial R}$$
$$=\frac{\partial}{\partial R}\left[G(R,R'')\,\frac{\partial G(R,R')}{\partial R}-\frac{\partial G(R,R'')}{\partial R}G(R,R')\right], \tag{2.53}$$

one finds

$$G(R'R'';E)-G(R''R';E)$$
$$=-\frac{\hbar^2}{2M}\left[G(R,R'',E)\,\frac{\partial G(R,R';E)}{\partial R}-\frac{\partial G(R,R'';E)}{\partial R}G(R,R';E\right]_0^\infty . \tag{2.54}$$

The expression $[\,.\,.\,.\,]_0^\infty$ vanishes because $G(R,R'';E)$ and $G(R,R';E)$ satisfy the same boundary conditions as a function of R when $R\to 0$ and $R\to\infty$. Equations (2.52) and (2.48) follow.

I. Numerical checks

The detailed balancing condition (2.48) is a useful check on two independent solutions of (2.30), with different inhomogeneous terms.

A second, independent check can be deduced from (2.30) if $\tilde{\xi}\to 0$ as $R\to\infty$; this is true if $\operatorname{Re}W(\infty)>E$. Multiply (2.30) by $\tilde{\xi}(R,k_i)$, integrate from $R=0$ to ∞, and subtract the complex-conjugate equation. Use the identity

$$\int_0^\infty dR\left(\tilde{\xi}^*\frac{\partial^2\tilde{\xi}}{\partial R^2}-\frac{\partial^2\tilde{\xi}^*}{\partial R^2}\tilde{\xi}\right)=\left(\tilde{\xi}^*\,\frac{\partial\tilde{\xi}}{\partial R}-\frac{\partial\tilde{\xi}^*}{\partial R}\tilde{\xi}\right)_0^\infty=0, \tag{2.55}$$

where we have used $\tilde{\xi}(0)=\tilde{\xi}(\infty)=0$. One finds

$$\int_0^\infty dR\,|\tilde{\xi}(R,k_i)|^2\Gamma(R)$$
$$=-2\int_0^\infty dR\,\operatorname{Im}\tilde{\xi}(R,k_i)\tilde{\zeta}(R,k_i)\tilde{\chi}_i(R). \tag{2.56}$$

This result gives a check on the absolute magnitude of $\tilde{\xi}$.

J. Cross sections

The cross sections follow from (2.12). In the total cross sections, the integration over the final direction of the electron leads to much simplification; therefore we shall consider them first.

If the dominant l value in the resonant amplitude is different from those taken into account in the potential amplitude, then the total cross sections (i.e., integrated over all final directions) contain no interference between the two terms in (2.13). According to the assumptions stated in Sec. II, this is the case in the ${}^2\Pi_g$ resonance in $e-\mathrm{N}_2$ scattering, so that in *this* case we may write for the total cross section for the production of a particular vibrational state

$$\sigma_{i\to f}=\frac{v_f}{v_i}\int d\hat{k}_f\,|T_{i\to f}|^2=\sigma^{\mathrm{res}}_{i\to f}+\sigma^{\mathrm{pot}}_{i\to f}, \tag{2.57}$$

where

$$\sigma^{\mathrm{res}}_{i\to f}\equiv\frac{v_f}{v_i}\int d\hat{k}_f\,|T^{\mathrm{res}}_{i\to f}|^2, \tag{2.58}$$

$$\sigma^{\mathrm{pot}}_{i\to f}\equiv\frac{v_f}{v_i}\int d\hat{k}_f\,|T^{\mathrm{pot}}_{i\to f}|^2. \tag{2.59}$$

A reciprocity relation for $\sigma^{\mathrm{res}}_{i\to f}$ follows from (2.58) with the aid of (2.48). The integral $\int d\hat{k}_f\,|T^{\mathrm{res}}_{i\to f}|^2$ is spherically symmetric with respect to $\hat{k}_i$, and may therefore be replaced by

$$\frac{1}{4\pi}\int d\hat{k}_i\,d\hat{k}_f\,|T^{\mathrm{res}}_{i\to f}|^2.$$

By comparing the definition (2.58) with the relation obtained by interchanging i and f, one finds

$$v_i^2\,\sigma^{\mathrm{res}}_{i\to f}=v_f^2\,\sigma^{\mathrm{res}}_{f\to i}. \tag{2.58$'$}$$

Since the principle of detailed balancing for the exact cross sections $\sigma_{i\to f}$ and $\sigma_{f\to i}$ is $v_i^2\sigma_{i\to f}=v_f^2\sigma_{f\to i}$, Eq. (2.58′) merely shows that our approximate method for calculating $\sigma^{\mathrm{res}}_{i\to f}$ is consistent with detailed balancing.

From (2.32) and (2.58),

$$\sigma^{\mathrm{res}}_{i\to f}=\frac{v_f}{v_i}\left(\frac{m}{2\pi\hbar^2}\right)^2\left[|\mathcal{Y}_{l(\mathrm{min})m(+)}(\hat{R},\hat{k}_i)|^2+|\mathcal{Y}_{l(\mathrm{min})m(-)}(\hat{R},\hat{k}_i)|^2\right]\cdot\left|\left(\chi_f\left|\,\tilde{\zeta}(R,k_f)\right|\frac{\tilde{\xi}(R,k_i)}{R}\right)\right|^2, \tag{2.60}$$

if one uses the orthonormality of the functions $\mathcal{Y}_{l(\mathrm{min})m(\pm)}(\hat{R},\hat{k}_f)$. Note that the interference between the $m(+)$ and $m(-)$ states has disappeared. [Differences in notation between this paper and Ref. 9 are explained in the Appendix.]

Expression (2.60) must still be averaged over the direction $\hat{R}$ of the axis; in the total cross sections, this average may be replaced by an average over $\hat{k}_i$. One obtains for the resonant cross section for the production of a particular vibrational state, integrated over all scattering angles,

$$\sigma^{\mathrm{res}}_{i\to f}=\frac{v_f}{v_i}\,\frac{m^2}{8\pi^3\hbar^4}\left|\left(\chi_f\right|\tilde{\zeta}(R,k_f)\left|\frac{\tilde{\xi}(R,k_i)}{R}\right)\right|^2. \tag{2.61}$$

The resonant differential cross section is obtained by averaging (2.12) [with (2.14b)] over molecular orientations $\hat{R}\equiv(\theta_R,\phi_R)$:

$$\left(\frac{d\sigma^{\mathrm{res}}}{d\Omega}\right)_{i\to f}=\frac{v_f}{v_i}\,\frac{1}{4\pi}\int d\hat{R}\,|T^{\mathrm{res}}_{i\to f}|^2. \tag{2.62}$$

Since the spherical harmonics in (2.32) are defined with respect to the molecular axis $\hat{R}$ as the polar axis [according to the remark after Eq. (2.26a)], all the angles appearing in (2.32) must be transformed to the laboratory frame before the integration (2.62); the observed scattering angles emerge explicitly from the transformation.

The spherical harmonics $\mathcal{Y}_{LM}(\hat{R},\hat{k})$, which are referred to the molecular frame, can be expressed in terms of the $\mathcal{Y}_{LM}(\hat{k})$, referred to the incident beam direction by the equation

$$\mathcal{Y}_{LM}(\hat{R},\hat{k})=\sum_{M'}\mathcal{D}^{L}_{M'M}(\omega)\mathcal{Y}_{LM'}(\hat{k})\,. \tag{2.63}$$

Here $\mathcal{D}^{L}_{M'M}(\omega)$ are the rotation matrices, defined by Rose,[44] and $(\omega)\equiv(\phi_R,\,\theta_R,\,\frac{1}{2}\pi)$ is the set of Euler angles which carries the frame defined by the incident beam direction into the frame defined by the internuclear areas. [The third Euler angle of the molecular frame is arbitrary for a diatomic molecule. We follow Van Vleck[45] and Hougen[46] by taking this third Euler angle equal to $\frac{1}{2}\pi$. Thus the Euler angles of the molecular frame are $(\omega)\equiv(\phi_R,\,\theta_R,\,\frac{1}{2}\pi.]$

Making use of (2.32), (2.63), and the orthogonality of the $\mathcal{D}$ functions, expression (2.62) reduces to

$$\left(\frac{d\sigma^{\text{res}}}{d\Omega}\right)_{i\to f}=\frac{v_f}{v_i}\,\frac{m^2}{64\pi^4\hbar^4}\left|\left(\chi_f\right|\tilde{\xi}(R,k_f)\left|\,\tilde{\xi}\,\frac{(R,k_i)}{R}\right)\right|^2 \cdot\sum_L A_L P_L\cos\theta, \tag{2.64}$$

with

$$A_L=(2L+1)(2l_{\min}+1)^2\begin{pmatrix} l_{\min} & l_{\min} & L\\ 0 & 0 & 0\end{pmatrix}^2 \times\sum_{m,m'}\begin{pmatrix} l_{\min} & l_{\min} & L\\ m & -m' & m'-m\end{pmatrix}^2, \tag{2.65}$$

where the sums extend over both values of m [i.e., $m(+)$ and $m(-)$]. Details of a similar analysis can be found for example in O'Malley and Taylor.[47]

The form of (2.64) suggests immediately that the differential cross section can be written as a product of the integrated cross section (which carries the energy dependence) and a normalized angular distribution $g(\theta)$ such that

$$\left(\frac{d\sigma^{\text{res}}}{d\Omega}\right)=\sigma^{\text{res}}_{i\to f}\,g(\theta)\,, \tag{2.66}$$

with

$$g(\theta)=\frac{1}{4\pi A_0}\sum_L A_L P_L(\cos\theta)\,.$$

In the case of the $^2\Pi_g$ resonance in N_2, $l_{\min}=2$, $m(\pm)=\pm1$, and the normalized angular distribution takes the explicit form

$$g(\theta)=(1/4\pi)\tfrac{15}{14}(1-3\cos^2\theta+\tfrac{14}{3}\cos^4\theta)\,. \tag{2.67}$$

III. RESULTS

Calculations have been done in the following stages:

(a) *Calibration of the* N_2^- *potential curve.* (Described in Sec. III A.) Calculated cross sections were fitted to experiment by adjustment of parameters in the N_2^- compound-state energy $W(R)$ in (2.3) and (2.10).

(b) *Tests of the parameters: new channels.* (Described in Sec. III B.) The parameters determined in (*a*) were used to calculate cross sections in channels other than those used in (*a*), which were then compared with experiment.

(c) *Tests of parameters: The total cross section.* (Described in Sec. III C.) The resonant cross sections for all channels $v=0\to 8$ were combined with cross sections for potential scattering to calculate total cross sections, which were compared with experiment.

(d) *Comparisons of parameters.* (Described in Sec. III D.) The parameters determined from (a) were compared with the *ab initio* calculations of Krauss and Mies,[10] and with previous parameter fits.

(e) *Calculation of cross-sections for vibrationally excited molecules.* (Described in Sec. III E) The parameters determined in (a) were used to calculate cross sections in vibrational channels which are still beyond the reach of experiment.

A. Calibration of the N_2^- potential curve

In Eq. (2.30) we write

$$W(R)=E^-(R)-\tfrac{1}{2}i\,\Gamma(R)\,, \tag{3.1}$$

where

$$E^-(R)\equiv\text{Re}\,W(R)\,. \tag{3.2}$$

The function $E^-(R)$ was represented by the Morse potential

$$E^-(R)=E^-(R_0^-)+D^-\{1-\exp[-(R-R_0^-)/a^-]\}^2\,, \tag{3.3}$$

and the function $\Gamma(R)$ by

$$\Gamma(R)=\Gamma(R_0)\frac{k(R)}{k(R_0)}\,\frac{v_2[k(R)\rho]}{v_2[k(R_0)\rho]}\,. \tag{3.4}$$

Equation (3.4) is the expression used by Blatt and Weisskopf[43] to represent the decay rate through a centrifugal barrier.

The quantities R_0^-, $E^-(R_0^-)$, D^-, $\Gamma(R_0^-)$, a^-, and ρ are adjustable parameters. The meaning of the first four is illustrated in Fig. 1. To see the significance of a^-, expand $E^-(R)$ in powers of $(R-R_0^-)$:

$$E^-(R)=E^-(R_0^-)+\tfrac{1}{2}M(\omega^-)^2(R-R_0^-)^2+\cdots\,. \tag{3.5}$$

The coefficient of the quadratic term contains

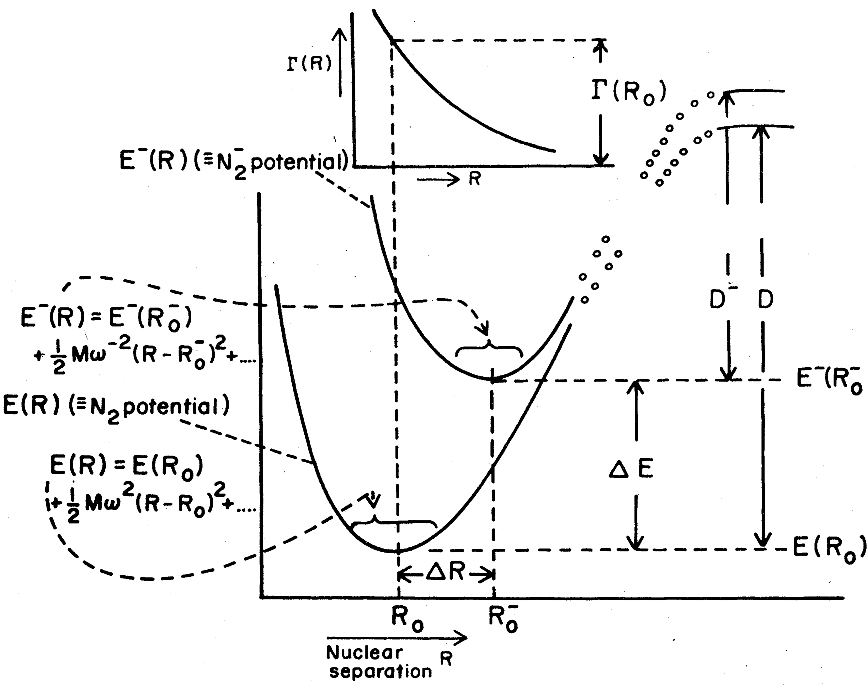

FIG. 1. Meaning of the adjustable parameters listed in Sec. IIIA.

$$\omega^- \equiv (1/a^-)(2D^-/M)^{1/2}; \qquad (3.6)$$

in the absence of autoionization (i.e., if Γ were zero), $\hbar\omega^-$ would be the vibrational spacing in N_2^-. M is the reduced mass of the nuclei. The parameter ρ is the radius, measured from the mass center of the molecule, beyond which we regard the extra electron as free. Beyond ρ, the extra electron feels only the centrifugal potential, but no potential from the molecule.

The wave number $k(R)$, which appears in (3.4), was calculated from

$$k(R) = (2m/\hbar^2)^{1/2}[E^-(R) - E(R)]^{1/2}, \qquad (3.7)$$

where $E(R)$ is the potential curve of the neutral N_2 molecule.

Cross sections were calculated by solving (2.30) for $\tilde{\xi}(R, k_i)$, using (2.61) for the cross sections integrated over angles, and (2.66) for the differential cross sections. The quantity $\tilde{\zeta}$, which appears in (2.30), (2.61), and (2.66), was expressed in terms of Γ by means of (2.25). The boundary condition at $R=0$ is $\tilde{\xi}(R=0, k_i)=0$, from (2.29), because the function $\xi_\pm(\vec{R}, \vec{k}_i)$ is finite for all $\vec{R}$. The boundary condition on $\tilde{\xi}$ as $R \to \infty$ depends on the energy and the value $W(R=\infty)$. In $e - N_2$ scattering in the neighborhood of the $^2\Pi_g$ shape resonance, one has $E - \mathrm{Re}\, W(\infty) < 0$, so that $\tilde{\xi}$ must vanish as $R \to \infty$.

The calculations were done with an initial choice of parameters which were physically reasonable. Small adjustments to the values of parameters were then made until the calculation fitted the energy dependence of the differential cross section for the excitation $v = 0 \to 1$ at 90°; the experimental curve used came from a recent measurement by Wong.[48] The absolute magnitude of the experimental curve was not used in this adjustment.

The initial estimates of the parameters were made in the following way: For $\Delta E \equiv E^-(R_0^-) - E(R_0)$, where R_0^- and R_0 are the equilibrium separations in $N_2^-(^2\Pi_g)$ and $N_2(X^1\Sigma_g^+)$, respectively: ΔE determines the smallest electron energies which lead to resonance scattering. A glance at the cross section curve for $v = 0 \to 1$ shows that $\Delta E \cong 1.8$ eV. For $\Delta R \equiv R_0^- - R_0$: ΔR can be estimated from neighboring molecular pairs, which differ by one π_g electron:

$$\Delta R(\mathrm{NO}^+, \mathrm{NO}) = 0.09\ \text{Å}, \quad \Delta R(\mathrm{O}_2^+, \mathrm{O}_2) = 0.085\ \text{Å}.$$

Therefore we expect $\Delta R(N_2, N_2^-) \cong 0.09$ Å. For $\Delta(\hbar\omega) \equiv \hbar\omega - \hbar\omega^-$: in neighboring molecular pairs, which differ by one π_g electron, one has

$$\Delta(\hbar\omega)(\mathrm{NO}^+, \mathrm{NO}) = 0.039\ \text{eV}, \quad \Delta(\hbar\omega)(\mathrm{O}_2^+, \mathrm{O}_2) = 0.037\ \text{eV}.$$

Therefore we expect $\Delta(\hbar\omega)(N_2, N_2^-) \cong 0.038$ eV, or $\hbar\omega^- \cong 0.26$ eV with $\hbar\omega = 0.293$ eV. For D^-: the dissociation limit of N_2^- should lie about 0.3 eV above the lowest dissociation limit of N_2, owing to the negative electron affinity of the N atom. With[49,50] a lowest dissociation limit for N_2 of 9.76 eV, one estimates $D^- \cong 8.4$ eV, if one includes a correction for ΔE and for the zero-point vibrational energy

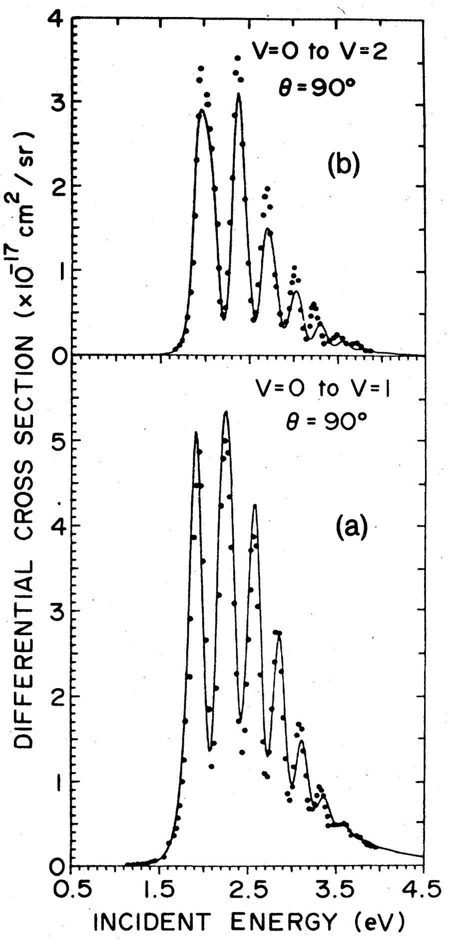

FIG. 2. (a) Differential cross section for the excitation $v=0\rightarrow 1$ at a scattering angle of 90°. •••••: Experimental absolute measurements by Wong *et al*; see Ref. 53. ———: Theoretical, calculated from (2.66), (2.61), (2.30), (2.25), and (2.28A), with the six parameters listed in Sec. IIIA and illustrated in Fig. 1, adjusted to give the best fit to the *relative* cross sections. The values of the parameters are given in column 2 of Table I. The absolute theoretical magnitude is then fixed without further adjustment of parameters (see Sec. IID). (b) Differential cross sections $v=0\rightarrow 2$ at 90° with the parameters in column 2 of Table I.

in N_2. For $\Gamma(R_0)$: the peaks in the energy dependence of the cross sections in different vibrational excitation channels $v=0\rightarrow v'$ shift from one v' to another in a systematic way. The "boomerang" explanation[27] of this phenomenon suggests that the average $\langle\Gamma\rangle$ of $\Gamma(R)$ over a vibrational cycle should be such that the lifetime $\hbar/\langle\Gamma\rangle$ is of the order of one vibrational period $2\pi/\omega^-$. This argument leads to $\langle\Gamma\rangle\approx 0.04$ eV. Since $\Gamma(R)$ decreases rapidly from $R=R_0^-$ outwards, because of the increase of the centrifugal barrier, one expects $\Gamma(R_0)$ to be somewhat larger; $\Gamma(R_0)\approx 0.2$ eV is a good first try.

For ρ: we chose $\rho=1.5$ Å, guided by the value $b=0.039\,13$ l/mol for the Van der Waals coefficient for N_2; that corresponds to a hard-sphere repulsion of two N_2 molecules at a separation of 3.14 Å between the mass centers.

The initial values of all parameters are collected in column 1 of Table I. After minor readjustments of the parameters, the fits shown in Figs. 2(a) and 2(b) were obtained for $(d\sigma/d\Omega)_{90^\circ}$ for $v=0\rightarrow 1$, $v=0\rightarrow 2$. The readjusted parameter values are given in column 2 of Table I. The fits in Figs. 2(a) and 2(b) compare experimental cross sections measured in absolute magnitude by Wong at Yale with our calculated cross sections, which are absolute too. The *relative* accuracy of the measurements in Figs. 2(a) and 2(b) at different energies is about ±10%; the *scale* of the experimental magnitudes has an accuracy of ±25%. The absolute magnitudes of the calculated cross sections are determined as soon as one has fitted the relative cross sections (see Sec. IID).

B. Tests of parameters: new channels

The *first test of the parameters listed in column* 2 *of Table* I was to calculate the cross sections for $v=0\rightarrow 3,4,5,6,7,8$. For comparison, we used the measurements made by Ehrhardt and Willmann; they were made absolute by normalizing the cross sections for $v=0\rightarrow 1$ and $v=0\rightarrow 2$ with Wong's experimental measurements in Figs. 2(a) and 2(b). We assumed that the relative experimental accuracy of the different channels was good enough for this normalization to make all measurements absolute. The experimental results are shown in Fig. 3, compared with cross sections calculated with the parameters in column 2 of Table I.

The *second test of the parameters listed in column* 2 *of Table* I was to compare new measurements of $(d\sigma/d\Omega)_{90^\circ}$ for $v=1\rightarrow 2$ with the cross sections calculated from the parameters determined in Sec. III/A, *without further adjustment*. The comparison is shown in Fig. 4(a). A similar calculation by another method, which attempts to use only a single adjustable parameter[51] is also shown in Fig. 4(b).

C. Test of parameters: total cross section

Measurements of the total cross section by transmission experiments have been made by Golden,[15] and more recently by Bonham and Kennerley[16] [Figs. 5(c), 5(a)]. The total cross section ($\equiv\sigma_T$) was calculated from the parameters in Sec. IIIA in accordance with Sec. IIJ by summing equation (2.57) over all final states. One finds (for $v=0$

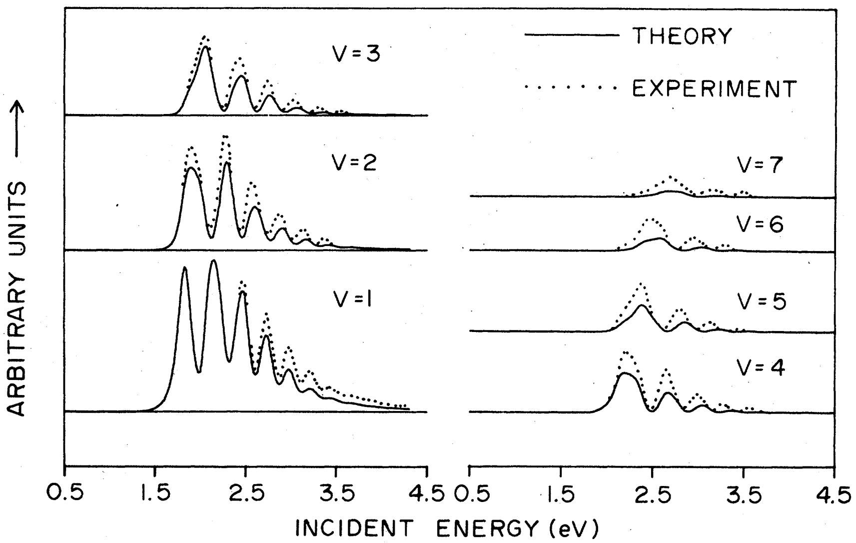

FIG. 3. Relative vibrational excitation cross sections. ••••: Experiment, from Ref. 14. ———: Theory, from the equations listed in the caption to Fig. 2(a), with the parameters in column 2 of Table I.

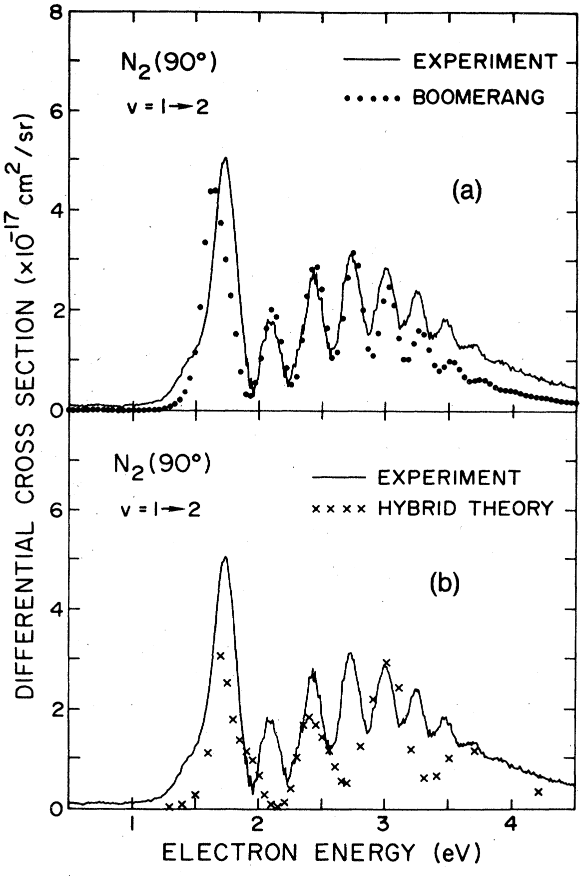

FIG. 4. (a) Differential cross sections at 90° for $v=1\to 2$, starting from a vibrationally excited state. ———: Experiment by Wong *et al*; see Ref. 48. ••••: Present theory, from the set of equations listed in the caption to Fig. 2(a), with the parameters listed in column 2 of Table I. (b) $v=1\to 2$, at 90°. ———: Experiment, as in Fig. 4a. xxxx: "Hybrid theory," Ref. 52.

in the initial state i)

$$\sigma_T=\sum_f \sigma_{0\to f}=\sum \sigma^{\mathrm{res}}_{0\to f}+\sigma^{\mathrm{pot}}_T . \qquad (3.8)$$

In σ^{pot}_T, we have retained only the vibrationally elastic component, for which we have used the *ab initio* calculation by Chandra and Temkin for the symmetries Σ_g, Σ_u, and Π_u. Figures 5(a) and 5(c) show that the two experiments agree with each other, if one smooths out the oscillations in Golden's measurements below 1.9 eV. The calculated cross section agrees with the experiments above 2.3 eV, but is about 20% too high below 2 eV. The resonant and potential contributions to the calculated σ_T are shown separately in Fig. 5(b) by dashed curves.

D. Comparison of parameters

The different sets of parameter values are compared in Table I. The comparison shows (i) The small magnitude of the readjustments from the first guesses in column 1 of Table I to the values giving the best fits, in column 2 of Table I. (ii) The good agreement between the values from the *ab initio* calculation in column 3 of Table I by Krauss and Mies[10] with the values for the best fit in column 2. (iii) The agreement between the best fit values from this (column 2) and the previous calculation (column 4). The only disagreement here is between the values of ρ, where we regard the previous value ($\rho = 3$ Å) as excessive. One parameter was quoted incorrectly in Ref. 9: the parameter A quoted in §3.1 of that paper should have been 0.088 eV, instead of the quoted value 0.03 eV. The error

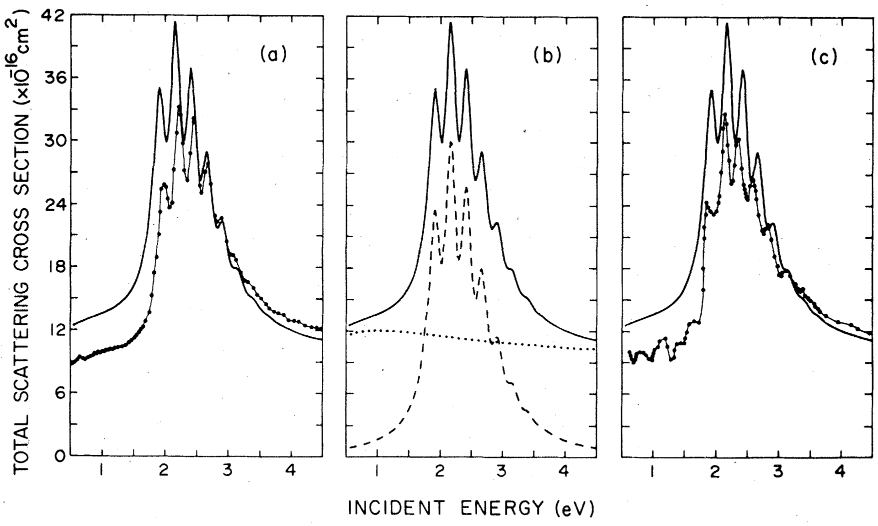

FIG. 5. (a) Total cross section σ_T. ●●●●: Measurements by Kennerley and Bonham Ref. 16. ———: Present calculation from (2.61), (2.30), (2.25), and (2.28a), with the parameters in column 2 of Table I, with the addition of a nonresonant cross section as in Eq. (3.8), from Ref. 26. (b) ———: Present calculation, as in (a). ------: Resonant contribution, calculated as in (a). ····: Nonresonant contribution, from Ref. 26. (c) ●●●●: Measurements by Golden, Ref. 15. ———: Present calculation, as in (a).

was pointed out by the late Professor Fiquet-Fayard. The point did not affect any of the other results in Ref. 9, because A was the last number to be worked out, from Eq. (11) of that paper.

E. Calculation of cross sections for vibrationally excited N_2 molecules

The parameters in Sec. IIIA have been used to calculate several cross sections for vibrational transitions. They are shown in Fig. 6 for inelastic, in Fig. 7 for superelastic, and in Fig. 8 for elastic collisions. [Only the resonant part of the cross section is shown in Fig. 8; the nonresonant part may be taken from Fig. 5(b).]

IV. DISCUSSION

The calculated results in Sec. III were derived from the picture of a bombarding electron trapped temporarily within the target molecule by a potential barrier due to the centrifugal potential. The molecular axis was held fixed during the scattering, and the extra electron regarded as free outside a sphere of molecular dimensions, about 3 Å in diameter. The trapped state of the extra electron is a quasistationary state of the kind introduced by Gamow[28] 50 years ago, matching onto outgoing waves outside the barrier, and therefore possessing a complex energy. (The term "Siegert state" is also used.[42])

The Born-Oppenheimer approximation (Sec. ID) enters with the assumption that the electronic Gamow state follows the slow motion of the nuclei adiabatically in a volume of molecular dimensions. This assumption reduces the determination of the nuclear wave function during the collision to the solution of a single ordinary differential equation (Sec. IIC); therefore it avoids the expansion in terms of vibrational target states which the "hy-

TABLE I. Parameter values.

	(1) Initial values	(2) Present calculation	(3) *Ab initio*, Ref. 10	(4) Previous fit, Ref. 9
$\Delta R \equiv R_0^- - R_0$ (Å)	0.09	0.0825	0.120	0.095
$\Delta E \equiv E^-(R_0^-) - E(R_0)$ (eV)	1.8	1.912	···	1.925
$\Delta\hbar\omega \equiv \hbar\omega - \hbar\omega^-$ (eV)	0.038	0.049	0.053	0.049
$\hbar\omega^-$ (eV)	···	0.244	0.24	0.244
D^- (eV)	8.4	11.961	13.04	11.961
$\Gamma(R_0)$ (eV)	0.2	0.54	0.80	0.57
ρ (Å)	1.5	1.41	···	3.0
a^{-a} (Å)	···	0.488	0.518	0.488
x^{-b}	···	0.0051	0.0046	0.0051

[a] Here $a^- \equiv (2D^-/M\omega^{-2})^{1/2}$, where M is the reduced mass.
[b] Here $x^- \equiv \hbar\omega^-/4D^-$.

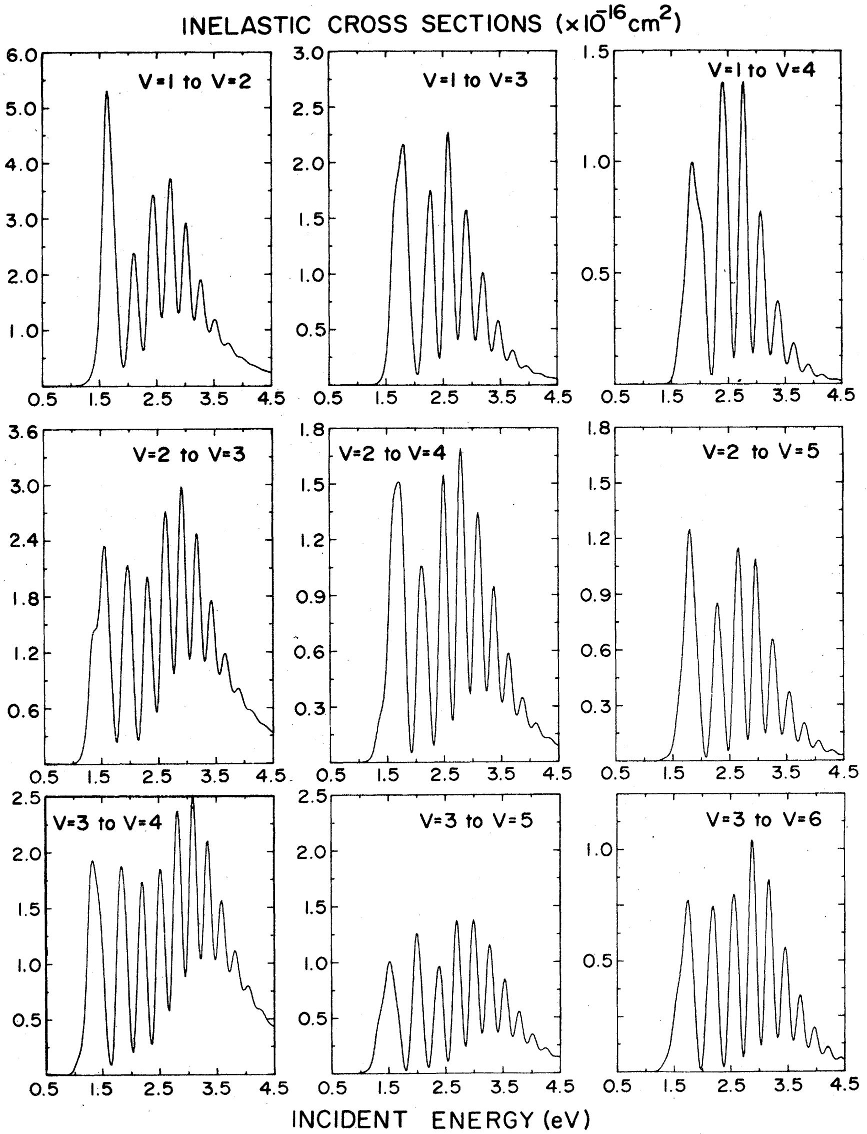

FIG. 6. Inelastic cross sections, integrated over final directions. (Note the different vertical scales.) Calculated with the parameters in column 2 of Table I.

brid theory"[26] used.

The assumption of adiabatic following when all the electrons are inside the molecule enables us to take into account the relaxation of the nuclear wave function during the collision; this relaxation is responsible[27] for the oscillations in the cross sections as a function of energy. By contrast, the frame transformation approach[38] ignores this relaxation.

The formal derivation of the theory now takes exchange into account (Sec. II G), by treating all electrons on an equal footing. The resulting cross sections are absolute, with the absolute magnitudes completely determined by the fit to the relative cross sections (Sec. II D). We have shown that the calculated cross sections automatically satisfy the principle of detailed balancing (Sec. II H).

The present calculations have put the boomerang approach to a much more severe test than the earlier ones[9]: we have determined (Sec. III) parameters in the theory by fitting the *relative* cross sections for $v=0\rightarrow 1$ and $v=0\rightarrow 2$ (Fig. 2), and then used these parameters to calculate other properties: the absolute magnitude (Fig. 2), the total cross sections (Fig. 5), the cross section $v=1\rightarrow 2$, which starts from an excited state (Fig. 4), and the excitation cross sections of vibrational levels up to $v=7$ (Fig. 3). Yet another test is the calculation of the pure rotational cross section, without vibrational excitation, which has been given in another paper.[52] Therefore the present paper has established that the combination of the boomerang method with parametrized potential

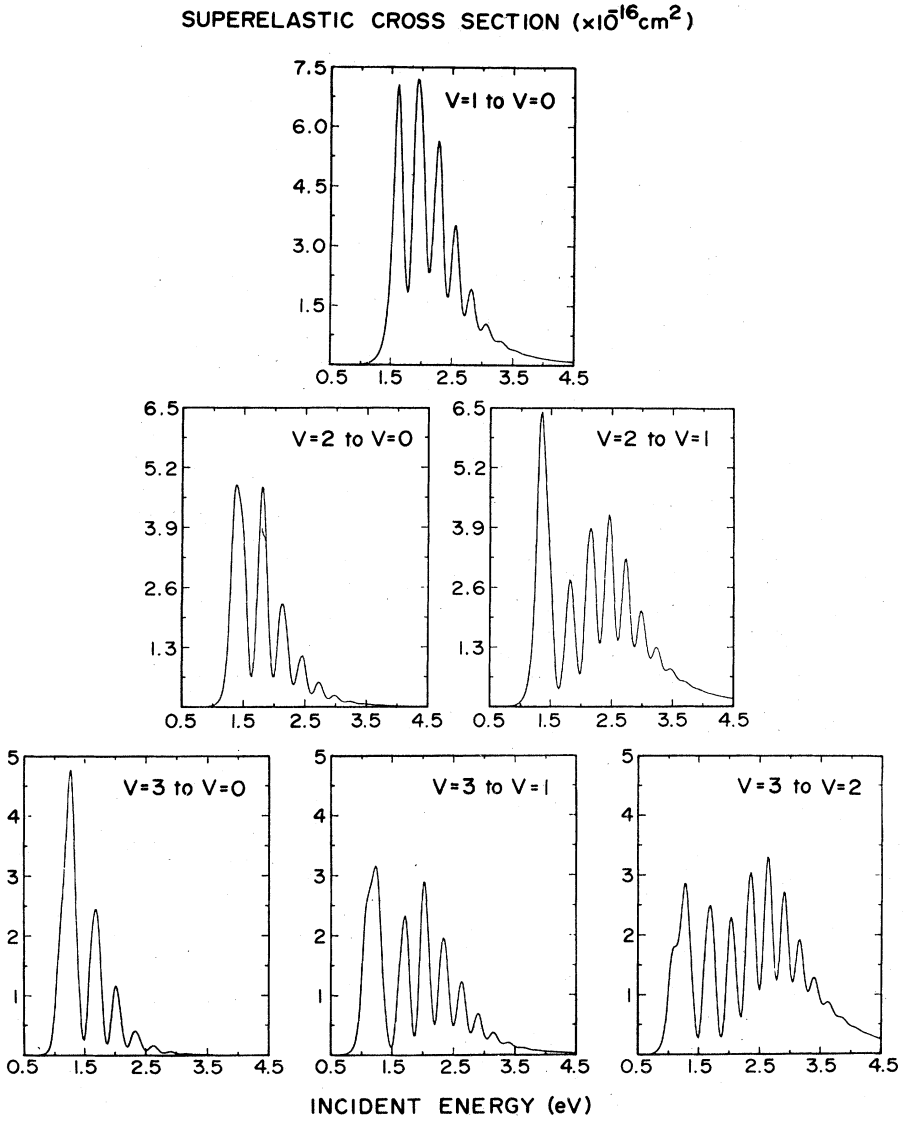

FIG. 7. Superelastic cross sections, integrated over final directions. (Note the different vertical scales.) Calculated with the parameters in column 2 of Table I.

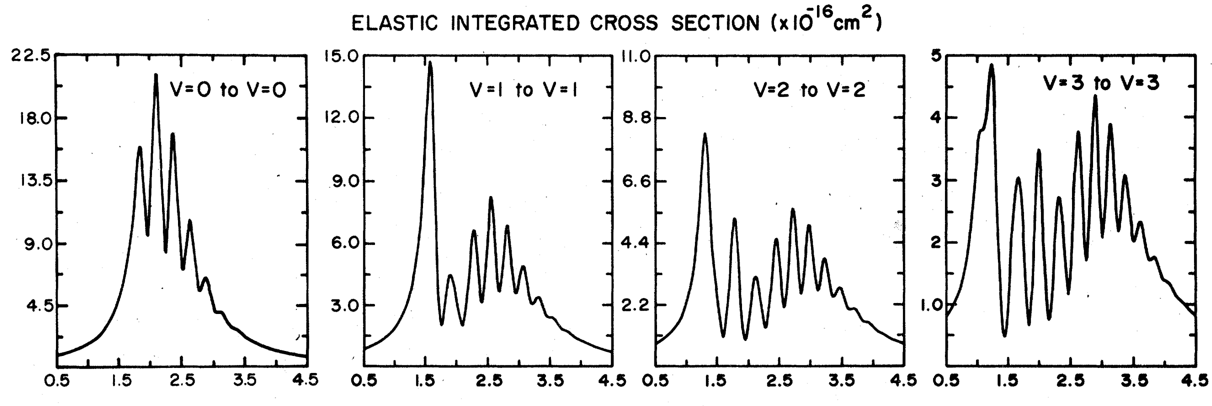

FIG. 8. Elastic cross sections, integrated over final directions; resonant component only. To obtain the complete elastic sections, add the nonresonant part from Fig. 5(b). Calculated with the parameters of column 2 of Table I. (Note the different vertical scales.)

curves is more than just a new description of known results: it enables one to use parameters determined from a small fraction of the experimental data to calculate many others, and obtain agreement with experiment.

The rotation of the axis has been ignored in this paper. The theory may be applied to rotational excitation by the rotational-impulse approximation, as has recently been done by Wong and Dubé.[52] Their work shows that the boomerang resonance responsible for the vibrational excitation also gives some rotational excitation with changes $\Delta J = 0, \pm 2$, or ± 4 in the angular momentum of the target molecule. Literature citations are given in Ref. 5.

Confrontation of experiment and *ab initio* theory in the present paper has been made by comparing the N_2^- potential curve we need to fit experiment in Sec. III with an *ab initio* calculation from Ref. 10. This procedure has the advantage that we can make very small adjustments in the potential curve, which have little effect on its shape, but which are crucial if the nodal structure of the nuclear wave function is to be reproduced with sufficient accuracy to agree with experiment. It is this freedom to make small adjustments in the potential curves which enables us to get the agreement shown in Sec. III.

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APPENDIX

Some changes in notation between Ref. 9 and the present paper have been made to simplify the analysis. The most important differences are: (i) A difference of a minus sign between the definitions of ζ' in (A8) of Ref. 9 and (2.11) of the present paper. (ii) A normalization factor $(2\pi)^{-3/2}$ in (A2) and (A16) of Ref. 9 has been dropped from the plane-wave states of initial and final electrons, as defined in Sec. II A in this paper. (iii) A factor $(4\pi)^{1/2}$ in (A13) and (A14) of Ref. 9 has been dropped from the corresponding equations (2.24a) and (2.29) of this paper. As a consequence of these changes, the expression for $\sigma_{i\to f}^{\text{res}}$ in (2.61) of this paper differs from Eq. (8) of Ref. 9 by a factor

$$[(2\pi)^{3/2}]^4\,[(4\pi)^{1/2}]^4 = 1064\pi^8 .$$

Thus in place of the factor $128\pi^5$ in Eq. (8) of Ref. 9 one finds the factor

$$128\pi^5/1064\pi^8 = 1/8\pi^3$$

in Eq. (2.61) of this paper.

The factors $(4\pi)^{1/2}$ and $(2\pi)^{3/2}$ mentioned in points (ii) and (iii) above account also for the different numerical factors in Eq. (14) of Ref. 9 and (2.23) and (2.24a) of this paper.

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