Scattering of slow electrons by molecules

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This review presents the current advances in the theory of collision of slow electrons with molecules. First the fundamental experimental results are reviewed. Then main attention is paid to the semiphenomenological and modeling approaches to the problem. The adiabatic approximation and its application to calculating elastic scattering cross-sections and cross-sections for rotational transitions are treated. The long-wavelength approximation (effective-range theory) is presented in greater detail. The problem is discussed of taking account of rotation in the collision process. In particular, a mechanism is revealed of formation of dipole resonances in the scattering of an electron by a rotating polar molecule. Different semiphenomenological methods are treated for calculating the resonance vibrational excitation of simple molecules. The quasiclassical representation for the cross-sections for vibrational transitions in the theory of Herzenberg is discussed. This representation is applied to analyze the process of dissociative recombination. The model is treated of emergence of a term into the continuous spectrum and it is applied to explain the threshold resonances in the vibrational excitation cross-sections of certain molecules. The role is discussed of dipole interaction in forming these resonances. The results of the theoretical calculations are compared with the experimental data.

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INTRODUCTION

From the applied standpoint, the most important fields of the physics of electron-molecule collisions are at present gas lasers and MHD (magnetohydrodynamic) energy converters. In high-power electric-discharge CO_2 lasers, vibrational-rotational excitation of CO_2 and N_2 molecules arises from these collisions; the N_2 molecules transfer their excitation in a resonance process to the asymmetric vibrational mode of the CO_2 molecule to create an inverted population. Thus the physics of gas lasers requires information on the cross-sections of inelastic vibrational-rotational transitions. Here the list of interesting molecules is already rather large and is continually expanding.

In MHD converters the fundamental problem involves determining the transport cross-section for collisions of electrons with polar molecules. The electric resistance of the plasma is considered to be mainly determined specifically by these collisions. The fundamental contribution to the transport cross-section comes from the peripheral elastic (or almost elastic, i.e., rotationally inelastic) collisions of electrons with molecules having very large cross-sections owing to the long-range nature of the interaction forces.

In describing the process of electron-molecule collision, it is convenient to distinguish three time scales. The electron shell of the molecule reacts most rapidly to the action of the incident electron (characteristic time τ_{el}). The vibrational-rotational subsystem reacts more slowly (characteristic

times $\tau_{\rm vib}$ and $\tau_{\rm rot}$):

$$\tau_{el} \ll \tau_{\rm vib} \ll \tau_{\rm rot}.$$

If the characteristic time of collision of the electron with the molecule proves to be substantially shorter than the vibrational time of the nuclei $\tau_{\rm vib}$, then the nuclei may be treated as being immobile in the course of the collision (fixed-nuclei approximation). In this case the entire physics of the process generally resembles the physics of collision of an electron with an atom. The fundamental difference is that the characteristics of the scattering become dependent on the nuclear coordinates. Since the experimental situation corresponds usually to a random distribution of the orientation of the molecules with respect to the direction of motion of the electron beam, in a theoretical treatment of the problem the effective scattering cross-section is averaged over all orientations of the molecules. Here one takes the internuclear distance as the equilibrium value. The obtained result is not the cross-section for pure elastic scattering, but corresponds to a summation over all final rotational states and yields no information on the cross-sections for vibrational excitation. However, one can calculate the amplitude of the vibrational-rotational transition by the formula

$$f_{n\gamma n_0\gamma_0} = \langle n\gamma | f\left(\{\mathbf{R}_\alpha\}; \ \mathbf{k}, \ \mathbf{k}_0\right) | n_0\gamma_0 \rangle. \qquad (\text{I.1})$$

Here γ_0 and γ are the set of rotational quantum numbers characterizing the initial and final states of the molecule, n_0 and n are the vibrational quantum numbers, $\{\mathbf{R}_\alpha\}$, $\alpha = 1, \ldots, N$, are the nuclear coordinates, and $\mathbf{k}_0$ and $\mathbf{k}$ are the initial and final momenta of the incident electron (here and below we use the atomic system of units).

Equation (I.1) is called the impulse or adiabatic approximation[1-4] and it permits one to derive a set of important consequences: the cross-section summed over the final rotational states is independent of the initial rotational state[5]; relationships exist between the cross-sections of different transitions.[6,7]

One must not neglect the vibrational dynamics in two cases: first, at energies of the electron close to the excitation threshold, at which the time of the process becomes comparable with $\tau_{\rm vib}$, and second, in the case of formation of an intermediate resonance state of the negative ion. The lifetime of such a complex is often comparable with the period of molecular vibrations (as, e.g., occurs in the case of the molecules N_2, CO, and CO_2), while it considerably exceeds this period in the O_2 molecule. An oscillatory structure in the cross-sections has been found in studying processes of this type.[1,150,166] Experimental study of the processes of resonance vibrational excitation involves the following difficulties:

1. Highly monokinetic electrons are required to resolve the vibrational-rotational structure.

2. It is difficult to identify the initial and final states of the target in studying transitions between excited vibrational-rotational states.

3. Most experiments do not yield absolute values of the cross-sections (or yield them with high error).

4. Many molecules of practical interest from the standpoint of MHD generation are chemically active in the gas phase, and experiments with them are difficult.

The theoretical description of resonance vibrational excitation is based on introducing the complex potential, which describes the capture of the electron into an intermediate state. This potential can be calculated from first principles (the theory of Bardsley[11]) or determined by semiempirical considerations (the model of Herzenberg[12]). An alternative approach is the R-matrix method,[10] in which the intermediate complex is calculated by the methods of quantum chemistry.

If the time of collision is comparable with the period of rotation of the molecule, then the rotational dynamics also becomes essential. In particular this pertains to polar molecules, owing to the long-range nature of the electron-molecule interaction. The most suitable apparatus for studying the problem is the theory of transformation of reference frames.[8,9] This field of study is as yet inaccessible to experiment, owing to the need of very highly monokinetic electron beams. Nevertheless, rotational transitions substantially influence the low-energy part of the distribution function of the electrons, and hence the study of these processes seems very important.

Below we shall review the fundamental experimental and theoretical methods of studying electron-molecule collision processes. The theoretical methods can be classified into three fields:

1. *Ab initio* calculations, which start directly with the many-particle Schrödinger equation in the Hartree-Fock approximation and with certain supplementary assumptions (pseudopotential allowance for exchange, static approximation with semiphenomenological allowance for the polarization interaction, etc.).

2. Semiphenomenological methods, which pose as their fundamental problem the reconstruction of certain quantum-mechanical characteristics of the process from a small number of experimentally available data, with subsequent calculation of the cross-sections of the experimentally unmeasurable processes.

3. Development of exactly solvable models which, along with relative mathematical simplicity, preserve various essential features of the physical situation and allow one to elucidate the role of the different physical assumptions adopted in the semiphenomenological approach.

The current literature contains several reviews[1-4] on the first—and to a considerably lesser degree—the second lines of approach. The studies along the third line have practically not been treated in review form. Without belittling the role of the first approach, let us point out, however, that such studies involve the development of several generations of complex programs that require high-power computers to realize them. We shall not discuss these studies in this review, while focusing attention mainly on the more physically lucid studies of the second and third approaches.

Being mainly interested in the fundamental side of the problem, we shall not be able to present all the theoretical and experimental results that have been obtained, but shall restrict the treatment only to illustrative material. We shall not treat processes involving electronic excitation and participation of positive molecular ions.

1. EXPERIMENTAL METHODS

Let us first take up the fundamental problems of the experimental methodology of determining the collision cross-sections of electrons with molecules. The following sections will present a detailed comparison of theory with experiment. Since this review does not treat processes with rearrangement of the electron shell, accordingly we shall not treat the problems involved with the study of optical excitation functions.

a) Beam experiments

1) The Ramsauer method

From the chronological standpoint, we should first touch upon the method of Ramsauer (see the review[13]), which essentially consists in determining the degree of attenuation of the intensity of an electron beam after it has passed through a chamber containing the gas being studied. The total cross-section for scattering of the electrons by molecules of the gas is found from the relationship

$$I = I_0 \exp\left(-\sigma_t nx\right). \tag{1.1}$$

Here I_0 is the initial electron current, I is the current of unscattered electrons, n is the density of the gas, and x is the path length over which the scattering of the beam occurs. The method has made it possible to measure the total scattering cross-sections of molecular hydrogen,[14,15] carbon dioxide,[13,16-18] and methane.[14] An advantage of the method is that it follows one relatively easily to obtain absolute scattering cross-sections, while its main defect is that it is applicable only to those molecules that exist in the gas phase at room temperature and are not chemically active.

To determine the differential scattering cross-sections requires introducing an electron analyzer into the apparatus to measure the current of electrons scattered at a given angle (see the review[19] and the references contained therein). Here the measurements yield only the relative differential cross-section, owing to difficulties of determining the effective path length.

The Ramsauer method gives large errors at low energies of the incident electron ($\lesssim 0.1$ eV) involving impaired energy resolution. In this region the time-of-flight methodology[20] is more effective; it reconstructs the energy spectrum from the electron time spectrum. The electron-scattering cross-sections of the CO molecule have been measured by this method.[20]

2) The method of crossed beams with analysis of the electron spectrum

A more refined method, which first became widespread in experiments on electron-atom scattering, is the crossed-beam method (for detailed discussion and references see the review[19]). Its advantage is the possibility of performing experiments with chemically active molecules. The measurements reduce to determining the spectrum and angular distribution of the scattered electrons as a function of their energy. The experimentally measured quantity—the number of scattered electrons detected at the angle θ per sec-

ond—is related to the differential cross-section by the formula

$$\frac{dN_e}{dt} = K(E) \sigma(\theta) \frac{S(\theta)}{v_M} . \tag{1.2}$$

Here $K(E)$ is the transmission efficiency of the detector, v_M is the velocity of the molecules in the beam, and $S(\theta)$ is a geometric correcting factor that amounts to the overlap integral between the flux of electrons and the flux of molecules in the collision volume. Although the dependence of S on θ has been studied rather well, it is highly difficult to determine its absolute value at low energies. Therefore the measurements usually yield relative cross-sections, while the absolute cross-sections are sought indirectly—by integrating the measured differential cross-sections and normalizing the obtained integral cross-section to the value found from another experiment or by theoretical calculation. Another method of normalizing consists in determining the ratio of the differential scattering cross-section at a given angle for the target being studied to that for a target for which it is well known.[21]

Another drawback of the crossed-beams method is the impossibility of measuring the elastic scattering cross-sections at small and large angles, and consequently, measuring the total elastic scattering cross-section. Hence one resorts to extrapolation in the region of small ($<20°$) and large ($>130°$) angles. In the former case one can do this by using the Born approximation, which works well for small-angle scattering when long range forces contribute substantially to the scattering. Extrapolation of the cross-sections into the high-angle region constitutes a more difficult problem. However, the large angles usually make a small contribution to the total cross-section.

The method has been employed to determine the differential cross-sections of "elastic" (summed over all final rotational states) scattering by the molecules LiF,[22] HCN,[21] KI,[23] CsCl,[24] and others and the vibrational-excitation cross-sections of the molecules H_2, N_2, CO, NO, O_2,[166] HF, HCl, HBr, H_2O, H_2S, CH_4, and SF_6.[185-188] In the case of the lightest molecule—H_2—analysis of the spectrum of scattered electrons enables one also to resolve the rotational structure and to obtain the cross-sections for the rotational and vibrational-rotational transitions.[25] In the case of heavier molecules one can observe only the broadening of the central peak associated with elastic scattering. It is a rather complicated problem to extract information from this on the cross-sections of rotational transitions, and this is impeded by the fact that the molecules in the initial state have different rotational angular momenta owing to the finite temperature. The first data[26,27] have recently begun to appear on resolving the rotational structure in the excitation of heavier molecules—N_2, CO, and H_2O.

3) The method of recoil of a molecular beam

In the beam recoil technique,[28] one does not measure the electron flux, but the flux of molecules deflected from the initial direction of motion by collision with electrons. The method allows one to obtain absolute cross-sections rather easily. However, it has a substantial defect involving the need to recalculate the differential scattering cross-section

of the molecules into the differential cross-section in the system of the center of mass. This procedure is very unstable, owing to the small deflection of the molecular beam in the laboratory system. In turn the latter involves the small ratio of the mass of the electron to the mass of the molecule. We should consider the attempt to determine by this method the differential cross-sections for electron scattering by the CsF,[29] CsCl,[30] and KI[31] molecules not to be very successful, since the recalculation of the cross-sections from the laboratory system to the center-of-mass system was quite incorrect.[2] If reliable methods of recalculation can be developed, this method holds good promise.

According to Ref. 29, yet another advantage of the method of molecular-beam recoil consists in the possibility of directly measuring the cross-sections of rotational transitions for heavy molecules. However, the preliminary results on rotational excitation of the CsF[32] molecule have not been subsequently published, and thus apparently they are incorrect.

b) Experiments with fluxes of thermal electrons (swarm experiments)

The methodology of beam experiments does not allow one to make measurements at very low energies of the incident electron (~ 0.01 eV). Therefore, for determination of the interaction cross-sections of molecules with electrons of thermal energy, one resorts to a different approach that consists in measuring the transport coefficients of the molecules under study in a weakly ionized gas (electric conductivity, heat conductivity, diffusion coefficient, etc.).

As the solution of the Boltzmann equation in the diffusion approximation implies, when one takes account of only the elastic collisions of electrons with gas molecules, the transport coefficients are related by an integral transformation to the diffusion cross-section $\sigma_d (v)$, where v is the velocity of the electron. For example, we obtain the following expression for the drift velocity of an electron in an electric field:

$$w = -\frac{4\pi}{3} \frac{F}{N} \int_0^\infty \frac{v^2}{\sigma_d (v)} \frac{df}{dv} \, dv. \qquad (1.3)$$

Here F is the applied electric field, N is the concentration of molecules, and f is the velocity distribution function of the electrons.

If we can consider f to be Maxwellian, then we can reconstruct $\sigma_d (v)$ from the experimental temperature-dependence of w (or any other transport coefficient). Since the direct solution of the integral equation (1.3) is difficult, one usually uses here a given analytic $\sigma_d (v)$ relationship (e.g., that following from the Born approximation or the effective-range theory) and reduces the problem to finding the parameters that enter into this relationship.

If there are no grounds for assuming that the distribution function is close to Maxwellian, then one must solve the Boltzmann equation taking into account various inelastic processes (as a rule, these are rotational and vibrational excitation) and calculate the transport coefficients from the found f. Here σ_d and the cross-sections for the inelastic processes are found by fitting the calculated values of the transport coefficients to the experimental. Thus the diffusion cross-sections and the cross-sections for rotational and vibrational excitation have been determined for the H_2, N_2, O_2, CO, and CO_2 molecules (see Refs. 33–35 and the references cited there).

However, in any case the applicability of the method is limited by the fact that Eq. (1.3) (and analogous formulas for the other transport coefficients) takes into account only elastic collisions. In the case of nonpolar molecules this approximation is reasonable. However, in the case of polar molecules the cross-sections for rotational transitions with change of the rotational quantum number by 1 or 2 are very large, and the assumption of dominance of elastic processes is inapplicable. Therefore the described method for polar molecules is applicable in the region of energies (and correspondingly, of temperatures) that are either small in comparison with the rotational constant or large in comparison with it but small in comparison with the vibrational energy of the molecules. In the latter case, an approximation adiabatic with respect to rotation holds, and one must take as σ_d the cross-section summed over all the final rotational states. This type of approach has been employed in Ref. 36 in processing the experimental data[37] on drift velocities of electrons in polar gases.

2. ELASTIC SCATTERING
a) Model potentials in the theory of elastic scattering

In proceeding to analyze the problem theoretically, we shall first treat the scattering of an electron by a molecule in the fixed-nuclei approximation. The problem is further simplified by assuming that the nuclei and electrons of the molecule give rise to a certain effective potential in which the incident electron moves, while the effect of the latter on the electrons of the molecule is neglected. This approximation is called the static approximation (or exchange-static, if one takes into account the exchange between the incident electron and the electrons of the molecule). The strong-coupling method has been developed[38–40] to allow for the polarization of the target under the action of the incident electron in the theory of electron-atom collisions. Systematic application of the strong-coupling method to the theory of electron-molecule collisions offers far greater difficulties of calculation. Therefore in this case one usually employs a simpler method—introduction of the semiphenomenological polarization potential. For example, in the case of a linear molecule it has the form

$$V_p (r) = -\frac{\alpha_0 + \alpha_2 P_2 (\cos \theta)}{2r^4} \left\{ 1 - \exp \left[\left(-\frac{r}{r_p} \right)^s \right] \right\}. \qquad (2.1)$$

Here we have

$$\alpha_0 = \frac{1}{3} (\alpha_\| + 2\alpha_\perp), \qquad \alpha_2 = \frac{2}{3} (\alpha_\| - \alpha_\perp),$$

while $\alpha_\|$ and $\alpha_\perp$ are the principal values of the polarizability tensor of the molecule. Without sufficient justification, the parameter s is usually taken equal to 6, while r_p is determined semiempirically, e.g., from the requirement that the resonance energy found theoretically must coincide with the experimental value.[41,42] Some more refined approaches are

the method of polarized orbits[43–46] and allowance polarization by using the Feynmam diagram technique.[47,48] We point out also Refs. 49–51, in which a polarization potential was used that contained no adjustable parameters.

As regards the static potential, one can calculate it in principle if one has the wave functions of the molecule. However, in the first stage of the treatment of the problem, it is convenient to have it in such a form as to obtain the solution analytically or at least to simplify substantially the numerical solution. Let us proceed to examine potentials of this type.

Let us assume that the interaction of the electron with the molecule is substantially different from zero only inside nonoverlapping spheres surrounding each nucleus. This approach is called the method of finite-range potentials (muffin-tin potential). The model allows an exact solution under the condition that one knows the scattering amplitudes at each of the spheres.[52,53] When applying the model to electron-molecule collisions, one can take these amplitudes from data on electron-atom scattering. The model of zero-range potentials (ZRP), which is obtained by letting the radii of the spheres approach zero, has enjoyed greater popularity. Evidently this approximation holds if, first, we can neglect the long-range component of the interaction (this requirement yields a lower bound on the energy of the incident electron) and, second, if the electron has an energy that makes the de Broglie wavelength large in comparison with the characteristic dimensions of the atoms contained in the molecule (this requirement yields an upper bound on the energy).

Scattering by a diatomic homonuclear molecule has been studied by the ZRP method by Subramanyan.[54] Exchange was taken into account by the method of Smirnov and Firsov.[55] Application of the ZRP method to more complex molecules and various generalizations of it have been discussed in detail in the book of Demkov and Ostrovskiĭ.[56]

In the ZRP approximation each well (atom) is characterized by one parameter. In order to make the model more flexible, one introduces potentials called separable potentials.[56] The superposition of a finite number of separable potentials has the form

$$\hat{V} = \sum_j |\varphi_j\rangle v_j \langle \varphi_j|.$$

Here the $|\varphi_j\rangle$ are Hilbert-space vectors.

The model of separable potentials belongs to the analytically solvable class, since the corresponding Schrödinger equation reduces to a linear algebraic system. The T-matrix method[57] is a further generalization.

One can also attain a substantial simplification by treating potentials that allow separation of the variables for the Schrödinger equation in some curvilinear system of coordinates.

First let us examine the potential of a point dipole:

$$V(r) = -\frac{D \cos \theta}{r^2}. \tag{2.2}$$

This can be used to study the scattering of an electron by a polar molecule.

In view of the long-range character of the potential in (2.2), the scattering by it is well described by the Born ap-

proximation.[58,59] The Born differential cross-section over the directions of the dipole-moment vector is

$$\sigma(\vartheta) = \frac{2D^2}{3k^2 (1 - \cos \vartheta)}. \tag{2.3}$$

Here ϑ is the angle between $\mathbf{k}_0$ and $\mathbf{k}$, where $\mathbf{k}_0$ and $\mathbf{k}$ are the initial and final momenta of the electron.

This implies that the diffusion cross-section (the cross-section for momentum transport) equals

$$\sigma_{\mathrm{d}} = \frac{8\pi D^2}{3k^2} \tag{2.4}$$

while the total cross-section diverges. This divergence, as well as the approach of σ_{d} to ∞ as $k^2 \to 0$, stem not from the Born approximation, but from the long-range character of the interaction.[60,61] They appear in all theories that treat scattering by a nonrotating polar molecule.

The treatment of the Schrödinger equation with the potential of (2.2) given in Ref. 65 leads to the appearance of additional features of the scattering by a point dipole. First a $D = D_{\mathrm{cr}} \equiv 0.6395$ exists such that, when $D > D_{\mathrm{cr}}$, the scattered particle is incident on the center (the same situation has been studied in Ref. 60 for the case of the spherically symmetrical potential a/r^2). This feature of the problem arises from the nonphysical behavior of the potential of (2.2) as $r \to 0$.

When $D > D_{\mathrm{cr}}$, another effect arises—an infinite number of bound states arises in the field of (2.2) that concentrate toward $E = 0$.[62–64] This effect involves not the behavior of the potential at zero, but, just like the divergence of the total cross-section, the long-range character of the potential.

In treating the problem with $D > D_{\mathrm{cr}}$, one often introduces a potential that reduces to (2.2) when $r > r_0$ and is a certain nonsingular function when $r < r_0$. The first calculations of electron scattering by polar molecules were performed in this way.[66–69] Moreover, one can introduce the potential of an impenetrable sphere for $r < r_0$.[70,71] All these methods have the defect that the result depends on r_0 and on the method of approximating the potential when $r < r_0$.

There is also an entire class of potentials that allow separation of the variables in the Schrödinger equation in prolate spheroidal coordinates. They were employed in the early calculations of scattering by the H_2, N_2, and O_2 molecules.[72,73] A general theory was developed by Abramov and Komarov.[74] An important special case is the potential of a finite dipole. Scattering by such a potential with allowance for symmetry, which allowed separation of the variables in prolate spheroidal coordinates, has been studied in Ref. 75. Here one obtains all the features of the problem of scattering by a dipole involving the long-range character of the potential.

b) The long-wavelength approximation (effective-range theory)

In the effective-range theory (ERT), the long-range part of the interaction is taken into as exact account as possible, while the account taken of the short-range action reduces to introducing a small number of parameters of the type of the scattering length and radius. This approach is valid if the de Broglie wavelength of the electron is large in comparison with the range of the short-range forces, i.e., the dimensions

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of the molecules. Hence the region of application of the ERT on the high-energy side is narrower in the case of nonpolar molecules than the region of application of the ZRP method. However, on the low-energy side the region of applicability of the ERT method is far broader. Moreover, the ZRP method is generally inapplicable to the case of polar molecules.

The behavior of the phases and amplitude of scattering by a short-range potential at low energies is well known. Now let us examine how these rules are modified when we take account of the long-range action. For simplicity we shall restrict the treatment to a linear molecule. Then the interaction potential of an electron with the molecule at large distances has the form

$$V(\mathbf{r}) \sim -\frac{DP_1(\cos\theta)}{r^2} - \frac{\alpha_0}{2r^4} - \left(\frac{Q}{r^3} + \frac{\alpha_2}{2r^4}\right) P_2(\cos\theta). \quad (2.5)$$

Here D is the dipole moment and Q the quadrupole moment.

The exchange potential falls off exponentially toward infinity, and hence is not taken into account in the expansion in (2.5). We can consider the terms of the multipole expansion of higher order to be effectively short-range.

1) Nonpolar molecules; comparison with experiment

For nonpolar molecules we have $D = 0$, and we must construct the low-energy expansion of the scattering amplitude for a potential that is equal to the following for $r > r_0$:

$$V(\mathbf{r}) = -\left(\frac{Q}{r^3} + \frac{\alpha_2}{2r^4}\right) P_2(\cos\theta) - \frac{\alpha_0}{2r^4}. \quad (2.6)$$

As is well known, the contribution of the potential of (2.6) to the scattering amplitude at low energies can be found using the Born approximation.[76–78] Hence the differential cross-section averaged over the directions of the molecular axis has the form

$$\sigma(\vartheta) = b^2 + \frac{gq}{4} + O(k^2), \quad q = 2k\sin\left(\frac{\vartheta}{2}\right), \quad (2.7)$$

$$b^2 = a^2 + \frac{4Q^2}{45}, \quad g = \pi\left(2\alpha_0 a + \frac{\alpha_2 Q}{15}\right).$$

Here ϑ is the scattering angle, and a is the scattering length.

In connection with the given result, we note that one can give a double definition of the scattering length: first, as $-\lim_{k\to 0}(\tan\delta_0/k)$, where δ_0 is the phase of the spherically-symmetrical scattering, and second, as $\sqrt{\sigma_0/4\pi}$, where σ_0 is the scattering cross-section at zero energy, while the sign of the scattering length in the latter case is the same as in the former. When $Q \neq 0$, these definitions do not coincide, since all the higher partial waves contribute to the cross-section at zero energy. In Eq. (2.7) and below we shall use the first definition.
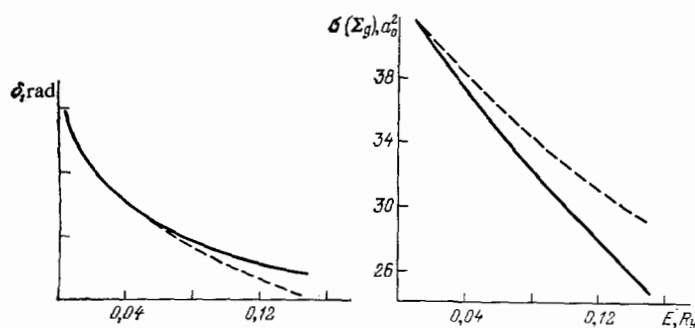
We obtain the following expressions for the total and the diffusional cross-sections:

$$\sigma_t = 4\pi\left(b^2 + \frac{gk}{3}\right) + O(k^2), \quad (2.8)$$

$$\sigma_d = 4\pi\left(b^2 + \frac{2gk}{5}\right) + O(k^2). \quad (2.9)$$

If $g < 0$, then the cross-section falls off with increasing energy near zero, and a minimum is observed at some k (the Ramsauer effect). Since usually we have $2\alpha_0|a| \gg \alpha_2|Q|/15$, the existence of a Ramsauer effect is governed, as in the case of scattering by an atom, by the sign of the scattering length.

To obtain the higher-order terms in the ERT expansion requires methods based on phase analysis of the amplitude. For the phase of scattering by the spherically symmetric potential $-\alpha_0/2r^4$, O'Malley et al.[79] have obtained

$$\tan\delta_0 = -ka - \frac{\pi}{3}\alpha_0 k^2 - \frac{4}{3}\alpha_0 ak^3 \ln k + O(k^3). \quad (2.10)$$

From this we find that the next term of the expansion (2.7)–(2.9) is not of the order of k^2, but of $k^2 \ln k$. The behavior of the phases for an angular momentum of the electron $l \geq 1$ depends only on the long-range action and is given correctly by the Born approximation[60]:

$$\tan\delta_l = \frac{\pi\alpha_0 k^2}{(2l-1)(2l+1)(2l+3)}. \quad (2.11)$$

The low-energy expansion of the reactance matrix K for the potential of (2.6) has been studied in Ref. 60. This type of expansion can be usefully employed in extrapolating the K-matrix into the region of very small energies, e.g., in order to determine the scattering length and to monitor the accuracy of numerical calculations. For example, processing of the results of the exchange-static calculations[81–83] yields respectively 1.83 and 2.17 for the scattering lengths for the molecules N_2 and H_2. Figure 1 shows the eigenphases and partial cross-sections for symmetry Σ_g in the case of scattering by the nitrogen molecule. The ERT data agree well with results of an exchange-static calculation[81] up to energies of 0.15 Ry (2 eV).

Now let us examine the results for the total and diffusion cross-sections. Figure 2 shows the data on scattering by the hydrogen molecule. The scattering length was determined by normalizing the expansion (2.8) to the result of the exchange-static calculation with allowance for polarization in the form of (2.1)[46] for $E = 0.2$ eV; it proved equal to 1.07. Thus, allowance for polarization diminishes the scattering length for H_2 by a factor of two. Just as in the case of the partial analysis, ERT yields good results up to 2 eV. The ZRP models and separable potentials yield a cross-section correct in order of magnitude, but do not reproduce the cor-

FIG. 1. Eigenphases and partial cross-sections (symmetry Σ_g) for e – N_2 scattering in the exchange-static approximation. Solid curves—data of Ref. 81, dotted curves—ERT results.[80]
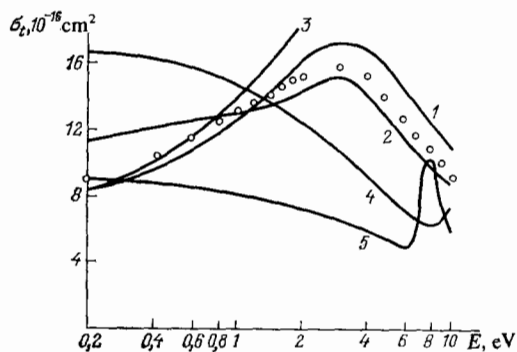
FIG. 2. Total elastic-scattering cross-sections of the H_2 molecule. 1, 2—exchange-static calculations with allowance for polarization in the form of a semiphenomenological polarization potential[46] and an optical potential[50]; 3—ERT [Eq. (2.8)]; 4—separable-potential approximation[84]; 5—ZRP approximation[56]; dots—experimental data.[15]

rect energy-dependence. This involves the lack of allowance for long-range action in these models.

Figure 3 shows the differential scattering cross-sections for the hydrogen molecule. The experimental data are normalized to the calculation[46] at $\vartheta = 90°$.

Figure 4 gives the diffusion cross-sections for the nitrogen molecule. The ERT data are normalized to the experimental data[85] for $k^2 = 0.01$. Naturally, the ERT does not reproduce the resonance of the form of symmetry Π_g at $k^2 = 0.2$ that has been observed experimentally and obtained theoretically in an exchange-static calculation with allowance for polarization.[86] This resonance had been detected even in the early calculations of Stier[72] and Fisk.[73]

Figures 5 and 6 show the total and diffusion scattering cross-sections for the CO_2 molecule. The ERT data are normalized to an experiment[34] with $E = 0.01$ eV. A scattering length of -7.39 is obtained for $Q = -3.86$.[42] Therefore a Ramsauer minimum is observed in the cross-section. The terms linear in k in the expansions (2.8) and (2.9) do not suffice for describing the behavior of the cross-section near the minimum. However, although the coefficient of $K^2 \ln k$ depends only on Q and α, the coefficient of the term of order k^2 depends also on the short-range force, and another adjustable parameter arises. Singh[87] has used this type of expansion for the CO_2, N_2O, and CO molecules. For CO_2 he obtained $\alpha = -7.2$. The large absolute value of the scattering

FIG. 4. Diffusion cross-sections for the nitrogen molecule. Solid curve—exchange-static calculation with allowance for polarization[86]; dotted curve—experiment[85]; dot-dash curve—ERT.

length of CO_2 was attributed to the existence of a virtual state near zero energy.[88]

We note also that a Ramsauer effect is observed in scattering by the methane molecule.[14] It has been reproduced in the calculations of Refs. 89 and 51.

In closing, let us present the data on quadrupole moments, polarizabilities, and scattering lengths for certain simple molecules as obtained by processing the best theoretical and experimental results by the ERT formulas. The references point out the source from which the cross-section data were taken (for the CO_2 molecule the results on scattering lengths were taken directly). The data on quadrupole moments and polarizabilities were taken from the same sources. We recall that the scattering length is related to the cross-section at zero energy by the formula $\sigma_0 = 4\pi (a^2 + 4Q^2/45)$ (see Table I).

2) Polar molecules

In order to construct an ERT for scattering by polar molecules,[90,91] one should take the solution of the Schrödinger equation with the potential of a point dipole (2.2) in the outer region, and then fit it to the inner solution by using the boundary conditions. In the simplest approximation the dependence of the scattering amplitude on the short-range force reduces to a single parameter analogous to the scattering length in the ordinary ERT. This approximation corresponds to reducing the short-range force to a zero–range
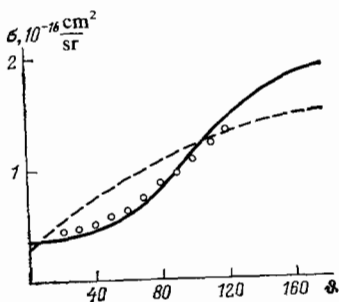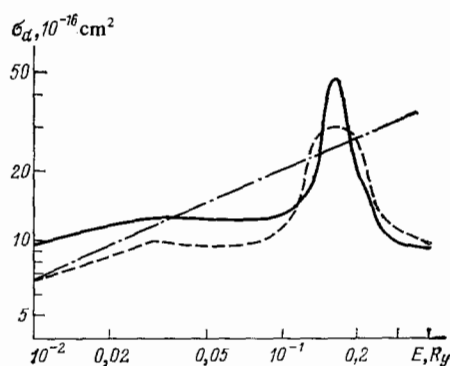

FIG. 3. Differential elastic-scattering cross-sections of the H_2 molecule at $E = 1$ eV. Solid curve—calculation of Henry and Lane[46]; dotted curve—ERT; dots—experimental data[25] normalized to the calculation[46] at $\vartheta = 90°$.
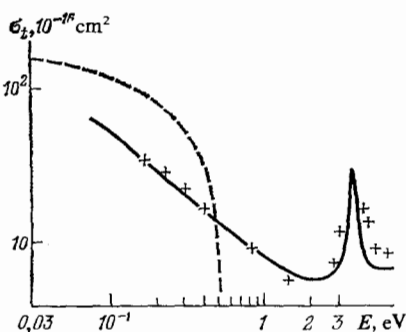

FIG. 5. Total scattering cross-sections for the CO_2 molecule. Solid curve—exchange-static calculation with allowance for polarization[42]; dotted curve—ERT; crosses—experimental data.[13,16-18]
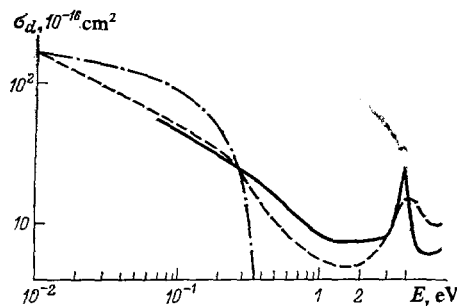
FIG. 6. Diffusion scattering cross-sections for the CO_2 molecule. Solid curve—calculation[42]; dotted curve—experiment[34]; dot-dash curve—ERT.

potential. The ERT formulas allow one also to obtain the following corrections.

The contribution of the quadrupole and the polarization interactions proves substantial when the parameters Qk and $\alpha_0 k^2$ become comparable with D. The case in which the increment to the dipole potential is spherically symmetric has been studied in Ref. 91, where a procedure was developed that makes possible a low-energy expansion of the S-matrix.

Calculation of the scattering cross-section of a polar molecule requires departing from the framework of the fixed-nuclei approximation. Therefore the results of the calculations will be examined in Sec. 3. In closing this section, let us examine the problem of bound states in the field of a polar molecule within the framework of the ERT.[92] When $D < D_{cr}$, the existence of a bound state depends on the magnitude of the short-range potential. When $D > D_{cr}$, there is an infinite number of bound states whose energies are given by the formula

$$E_n = -\frac{1}{2} \exp\left[-\frac{\pi(2n+1)+\alpha}{\mu} \right], \quad n = 0, 1, \ldots$$
(2.12)

Here μ depends on D, while α is the sole parameter of the theory that depends on the short-range force.

We have dropped negative values of n, since the corresponding E_n values do not satisfy the condition of applicability of the ERT. On the side of energies of low absolute magnitude, the number of roots is restricted by the lack of applicability of the fixed-nuclei approximation. According to the criterion of Crawford and Garrett,[93] a bound state actually exists if the affinity energy calculated in the Born-Oppenheimer approximation is larger than $(1/12–1/10) \times B_r$, where B_r is the rotational constant (under the condition that the rotational angular momentum of the negative ion is zero).

One can find the parameter α by Eq. (2.12) from the experimental value of the energy of the bound state of the negative ion; this allows one to determine the scattering amplitude. According to Ref. 94, this procedure can be called a generalized quantum-defect theory for the interaction of the electron with the polar molecule. However, it often turns out that not a single bound state exists at all, even when $D > D_{cr}$ (e.g., in the case of the HF and H_2O molecules). Then it can prove useful to calculate theoretically the electron affinity energy of the molecule, as reproduced formally in the Born-Oppenheimer approximation.

3. ROTATIONAL TRANSITIONS

a) The long-wavelength approximation for nonpolar molecules

In principle all the methods presented in Sec. 2 can be used for calculating the cross-sections for rotational transitions by Eq. (I.1). The application of the ZRP method has been examined in the book of Ref. 56. The cross-sections of rotational transitions with excitation of electronic states of the molecule have also been studied by this same method.[95] Since the ZRP method does not take the long-range force into account it becomes inapplicable at low enough energies of the electron. At the same time, the long-wavelength approximation yields a result whose applicability as $k \to 0$ is limited only by the adiabatic approximation.

For simplicity, we shall treat everywhere below the case of a linear molecule in a Σ state. Then the rotational wave functions reduce to spherical harmonics. A generalization of the theory of rotational transitions to nonlinear molecules has been given in Ref. 96.

The cross-section for rotational excitation differs from zero only for transitions $j_0 + 2 \leftarrow j_0$, and it has the form

$$\sigma_{jj_0} = \frac{8\pi}{15} \frac{(j_0+1)(j_0+2)}{(2j_0+1)(2j_0+3)} \left(Q^2 + \frac{\pi}{4} \alpha_2 Qk \right) + O(k^2). \quad (3.1)$$

According to (3.1), the cross-section increases or falls off with increasing energy near the threshold, respectively if $Q > 0$ or $Q < 0$. In the latter case a minimum is observed in the cross-section.

Figure 7 shows the data on the differential cross-sections for the $1 \leftarrow 1$ transition in the H_2 molecule for $E = 1$ eV.

In order to generalize Eq. (3.1) into the energy region where the adiabatic approximation is inapplicable, one must calculate the Born integral with allowance for the change in the absolute magnitude of the momentum of the electron in the collision process. As a result we have[98–100,77]

TABLE I.

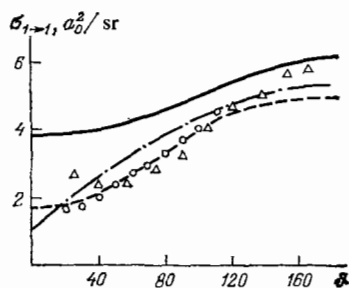| Molecule	Q	α_0	α_r	a_{theor}	a_{exp}
H_2	0,48	4,52	1,38	1,07 [46]	1,12 [15]
N_2	—0,935	11,9	4,2	0,75 [86]	0,55 [85]
CO_2	—3,86	17,9	9,2	—6,17 [88]	—7,2 [87]
CH_4	0	17,5	0	—3,1 ÷ —3,3 [51]	

FIG. 7. Differential scattering cross-sections for the hydrogen molecule in the state with $j = 1$ at $E = 1$ eV. The data are given from Ref. 56 with addition of the ERT results (dot-dash curve). Solid curve—calculation in the ZRP approximation; dotted curve—static approximation with allowance for polarization[97]; symbols—experimental data.[14,25]

FIG. 9. Cross-sections for rotational excitation of the nitrogen molecule (transition $j = 0 \rightarrow 2$). Curves $R = 1.75$; $R = 1.80$—calculations in the distorted-waves approximation[102] with different choices of the cutoff parameter in the long-range potential; GS—Eq. (3.2) with $\alpha_2 = 0$; DM—with $\alpha_2 \neq 0$ (data taken from the review of Ref. 1).

$$\sigma_{jj_0} = \frac{8\pi}{15} \frac{(j_0+1)(j_0+2)}{(2j_0+1)(2j_0+3)} \left[Q^2 \frac{k_j}{k_{j_0}} + \frac{\pi\alpha_2 Q}{16} \left(3k_j + \frac{k_j^3}{k_{j_0}^2} \right) \right.$$

$$\left. + \frac{9}{1024} \pi^2\alpha_2^2 \left(k_{j_0} k_j + \frac{k_j^3}{k_{j_0}} \right) \right],$$

$$j = j_0 + 2. \tag{3.2}$$

The expression (3.2) for $\alpha_2 = 0$ is called the Gerjuoy-Stein formula,[98] and the Dalgarno-Moffett formula for $\alpha_2 \neq 0$.[99] In contrast to (3.1), it is not asymptotically exact in nature, but is a reasonable extrapolation into the region of small k_j. For example, the excitation cross-section approaches zero at the threshold, in accord with the Wigner law.[101]

Figs. 8 and 9 illustrate the application of Eq. (3.2) to processes of rotational excitation of H_2 and N_2 molecules. Since $Q < 0$ for N_2, the cross-section passes through a minimum.

b) Scattering by polar molecules at energies greater than the rotational constant

1) Regulation of the total cross-section[90]

By applying Eq. (I.1) to polar molecules, one can obtain the amplitude and differential cross-sections of rotational transitions. However, the total cross-section for $j = j_0 \pm 1$ diverges. This involves the already mentioned inapplicability of the impulse approximation. In order to eliminate this
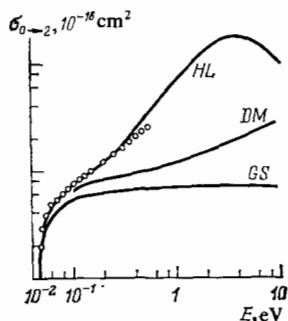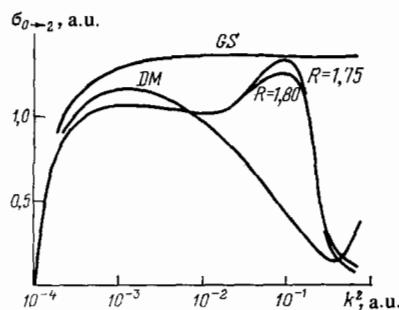

FIG. 8. Cross-sections for rotational excitation of hydrogen molecules (transition $j = 0 \rightarrow 2$). HL—exchange-static calculation with allowance for polarization[46]; GS—Eq. (3.2) with $\alpha_2 = 0$; DM—Eq. (3.2) with $\alpha_2 \neq 0$; dots—experiment[35] (data taken from the review of Ref. 1).

divergence, let us first examine expansion of the total cross-section in partial waves having different projections of the angular momentum of the electron:

$$\sigma_t = \sum_m \sigma_t^{(m)}. \tag{3.3}$$

In order to elucidate the nature of the convergence of this series, we can calculate $\sigma_t^{(m)}$ in the Born approximation[36,90]:

$$\sigma_{tB}^{(m)} = \frac{4\pi D^2}{k^2} [2m^2\psi'(|m|) - 2|m| - 1],$$

Here ψ' is the derivative of the digamma function.

This implies that the series in (3.3) diverges as a harmonic series. Classical considerations imply that the fixed-nuclei approximation becomes inapplicable at $|m| > k^2/jB_r$ (when $j = 0$, the denominator contains a quantity of the order of B_r). On the other hand, the Born approximation becomes applicable when $|m| > \sqrt{D}$. Hence, when $k^2 > jB_r\sqrt{D}$, one can use the Born approximation with allowance for rotation to remove the divergence of the series in (3.3). The result has the form

$$\sigma_{tj_0}(B_r) = \sum_m [\sigma_t^{(m)}(0) - \sigma_{tB}^{(m)}(0)] + \sigma_{tB}(B_r).$$

Here $\sigma_{tj_0}(B_r)$ denotes the scattering cross-section of a molecule having the rotational constant B_r and the angular momentum j_0 in the initial state:

$$\sigma_{tj_0}(B_r) = \sum \sigma_{jj_0}.$$

The expression for σ_{j_0} in the Born approximation has the form[103]

$$\sigma_{jj_0}^B = \frac{8\pi}{3} \frac{D^2}{k_{j_0}^2} \frac{j_>}{2j_0+1} \ln \left| \frac{k_{j_0}+k_j}{k_{j_0}-k_j} \right|. \tag{3.4}$$

Here we have $j = j_0 \pm 1$, and $j_> = \max(j_0, j)$.

Equation (3.4) indicates a logarithmic divergence of the total cross-section as $B_r \rightarrow 0$, i.e., approach to the impulse limit.

An alternative procedure for regularizing the total cross-section consists in an analogous subtraction of the differential cross-sections when integrating them over the scattering angle.[2]

2) Classical and semiclassical methods

The classical method enables one to derive relatively simple formulas for the scattering cross-sections of electrons by model potentials. Since the classical approach is valid when a large region of impact parameters contribute to the cross-section, it has been applied mainly to the problem of scattering by polar molecules.

Dickinson and Richards[104] have treated transitions in a polar molecule for $|\Delta j| = 1$ in the impact-parameter approximation. They use the model of Seaton[105] with account taken of unitarity and of the finite dimensions of the molecule. The following expression was obtained for the diffusion scattering cross-section at low energies[106]:

$$\sigma_d = \frac{\pi^2}{16k^2}\left(19D - \frac{3\pi}{8}\right).$$ (3.5)

F. T. Smith and his associates[107–109] have employed the method of the classical S-matrix theory[110] for scattering by dipole and quadrupole potentials. The method enables one to obtain the cross-sections for transitions between states having different rotational quantum numbers. However, since the molecule is treated classically, the expressions for the cross-sections are valid only at large enough j. The semiclassical approach[111,112] lacks this defect; according to it one treats the classical S-matrix in the fixed-nuclei approximation, and then employs the adiabatic approximation (I.1) for calculating the matrix elements. This implies the following expression for the total cross-section for rotational excitation:

$$\sigma_{j0} = \frac{8\pi D^2}{3k^2}\frac{2j+1}{(j-1)\,j\,(j+1)\,(j+2)}, \quad j \geqslant 2,$$
$$\sigma_{00} = \frac{8\pi D^2}{3k^2}\left(\ln 2 - \frac{1}{4}\right).$$ (3.6)

When $j = 1$, one can regularize the cross-section by the same methods as for the quantum-mechanical cross-section, i.e., examine the region of large impact parameters with account taken of rotation.

An oscillating dependence on the parameter $D\sin(\vartheta/2)$ appears in the differential cross-section owing to interference of the classical trajectories. An analogous effect arises in calculating the Glauber scattering amplitude by the stationary-phase method.

Equations (3.5) and (3.6) are simple enough and at the same time yield a non-zero result for $j \neq 0$ (in contrast to the Born approximation).

3) Results and comparison with experiment

Let us examine the results of calculations for certain molecules.[92,113] The electron-affinity energy of the LiF molecule is 0.33 eV.[144] Then Eq. (2.12) implies that $\alpha = 2.42$, and that there are two more bound $^2\Sigma^+$ states of LiF$^-$ having energies of 0.495×10^{-2} and 0.74×10^{-4} eV (the latter energy is of the order of B_r and hence must be calculated with allowance for rotation). The different methods of calculating the total cross-sections for rotational transitions have been compared in Refs. 2 and 84. The results of the different approaches agree rather well with one another, which indicates the applicability of the simple methods (the semiclassi-
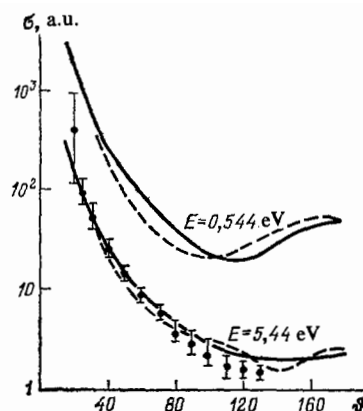

FIG. 10. Differential scattering cross-sections for the LiF molecule. Solid curves—ERT data[113]; dotted curves—exchange-static calculation[2]; dots—experimental data.[22]

cal and ERT methods) for calculating the scattering by molecules having a large enough dipole moment.

Figure 10 shows the total differential scattering cross-sections of LiF at $E = 0.544$ eV and 5.44 eV, and gives the comparison with experiment.[22] Figure 11 presents the data on scattering by the HCN molecule. An estimate of the electron-affinity energy of HCN in the Born-Oppenheimer approximation[115] implies that $3.8 < \alpha < 4.55$. As we see from Fig. 11, this agrees well with the experimental data on the differential cross-sections.[21]

In principle the ERT can be applied to all polar molecules for which one knows the electron affinity as calculated in the fixed-nuclei approximation. For example, although bound states of the HF$^-$ and H$_2$O$^-$ ions do not exist, estimates are known of the affinity energy as calculated in the Born-Oppenheimer approximation.[115] They can be used to calculate the scattering cross-sections of the HF and H$_2$O molecules.[92]

On the other hand, if a molecule possesses a large dipole moment ($\gtrsim 3$), then the total and diffusion cross-sections depend weakly on the parameter α, and one can obtain good
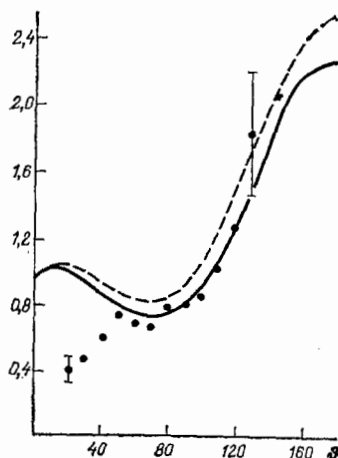

FIG. 11. Ratio of the differential scattering cross-section for the HCN molecule to the Born scattering cross-section for this molecule at $E = 3$ eV. Curves—ERT data[113]; solid curve—for $\alpha = 4.64$; dotted curve—for $\alpha = 5.30$. Dots—experimental data.[21]

estimates for the cross-sections without fixing the value of this parameter more precisely.[90] For example, we obtain the following expressions for scattering by CsF at $E = 1$ eV (in units of πa_0^2):

$$105 < \sigma_d < 125,$$
$$2287 < \sigma_t < 2297, \quad j = 41,$$

on the other hand, the Born approximation yields $\sigma_d = 350$ and $\sigma_t = 2681$, while the strong-coupling method yields $\sigma_d = 117$ and $\sigma_t = 2276$.

c) Theory of transformation of reference frames

All the methods described above rest on the approach of the molecular frame of reference (MFR) (*molecular frame* or *body frame* in the English-language literature), in which a vector rigidly fixed to the molecule is taken as the singled-out direction (e.g., in a linear molecule it is the internuclear vector). The calculation of the collisional dynamics is performed in this frame, while the transformation to the laboratory frame of reference (LFR) is performed either by Eq. (I.1) or by averaging the cross-section over all orientations of the molecule. In the latter case one obtains a cross-section summed over all final rotational states.

The above-described regularization of the integral cross-section for scattering of an electron by a polar molecule has required going outside the framework of the MFR approach. In general, when one goes outside the framework of the adiabatic approximation, the LFR approach is more suitable. The most general method consists in expanding the total wave function of the electron-molecule system in the rotational states of the molecule and then solving the system of strong-coupling equations.[116]

However, the LFR representation possesses a number of defects, though permitting one relatively simply to allow for rotation of the molecule. First, the structure of the strong-coupling equations in the LFR representation is far more complex than in the MFR representation. Second, the calculation of the matrix of exchange integrals in the LFR representation involves considerable difficulties. Upon taking this into account, Fano and Chang[8,9] have proposed a theory of transformation of frames of reference. Here one introduces the radius r_1 such that, when $r < r_1$, the interaction of the electron with the molecule is far larger than the rotational constant. Then, when $r < r_1$, one can neglect the rotational splitting and solve the system of equations in the MFR representation, while using the fixed-nuclei approximation. When $r > r_1$ one must take the rotational splitting into account and solve the problem in the LFR representation. The fitting of the functions in the different regions is carried out by using the unitary matrix found by Fano.[8] Since we usually have $r_1 > r_0$, where r_0 is the range of the short-range force, then, when $r > r_1$, the system of equations in the LFR representation has a relatively simple form, and its numerical integration presents no substantial difficulties.

One can also transform the frames of reference in angular-momentum space. This procedure has actually been done in regularizing the integral cross-section for scattering by a polar molecule (Sec. 3b,1).

d) Scattering by a polar molecule at energies of the order of and less than the rotational splitting

Let us study the scattering by a polar molecule at energies of the order of and less than the rotational splitting jB_r. The interest in this region arises in part from the fact that dipole resonances can occur in it above the threshold that usually do not arise in theories not allowing for the rotational splitting.[117] This problem has been studied by using the LFR approach throughout all space.[118,119] However, as we have pointed out above, this approach has a number of defects that are removed by transforming the frame of reference. Let us study the application of this method within the framework of the ERT.[120] Since this is a multichannel problem, it is convenient to introduce the sum of the eigenphases δ_{sum} for analyzing the results.

Further, we shall assume that $D > D_{cr}$. Then, in the fixed-nuclei approximation an infinite number of bound states exists. Accordingly δ_{sum} increases without bound as E approaches zero, by increasing by π an infinite number of times. On the other hand, when $E \ll B_r$, the adiabatic approximation is inapplicable, and elastic scattering in the channel $j = 0$ is described with good accuracy by the polarization potential $-\alpha_d/2r^4$.[121] Here α_d is the effective dipole polarizability arising from the coupling of the states $j = 0$ and $j = 1$,

$$\alpha_d = \frac{D^2}{3B_r}.$$

Then the tangent of the scattering phase approaches zero as $E \to 0$ according to (2.10) and (2.11). Consequently, when $E = 0$ we have $\delta_{sum} = N\pi$, where N is an integer.

Equation (2.10) implies that, when $l = 0$ and $a < 0$, δ increases, starting with $E = 0$. At some value of E that depends on B_r and the total angular momentum J, it undergoes a jump, while "adjusting" itself to the adiabatic value δ_{sum}^{ad}. In the region of the jump the phase increases in resonance fashion, owing to scattering by the virtual level.[60] When $l \geqslant 1$, the resonance behavior of the phase arises from scattering by a quasidiscrete level. The corresponding resonance is a shape resonance. Its existence involves the presence of a dipole interaction in the inner region and a centrifugal barrier in the outer region.[119] Finally, when $l = 0$, $a > 0$, the phase rapidly decreases, and we have resonance scattering by a bound state.[60]

One can approach the same problem from the standpoint of the analytical theory of the S-matrix. When $B_r = 0$, the S-matrix has a finite number of poles that lie on the real negative semiaxis of the complex energy plane and are determined by Eq. (2.12). When $B_r \neq 0$, almost all the poles leave the real axis and lie on a nonphysical sheet of the Riemann energy surface. (This process has been discussed in Refs. 122 and 123 for the case of scattering by a helium atom). If $l = 0$, then the poles lie on the real axis of the nonphysical sheet and correspond to virtual states, while when $l \geqslant 1$, the poles are complex and correspond to quasidiscrete states. Several poles can remain on the physical sheet, which corresponds to the conservation of bound states. According to the Crawford-Garrett criterion,[85] the states are conserved for which $\mathscr{E}^{ad} \geqslant (1/12-1/10) B_r$, where $\mathscr{E}^{ad}$ is the energy of affinity of

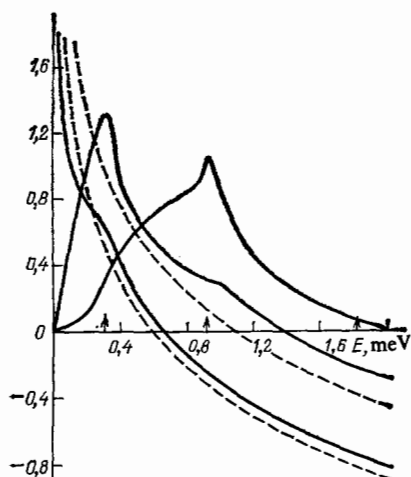A. K. Kazanskiĭ and I. I. Fabrikant   617

FIG. 12. Sums of eigenphases (apart from a term $N\pi$) for scattering by the LiF molecule. The numbers denote the value of J. The dotted curve indicates δ_{sum} in the adiabatic approximation. The arrows indicate the thresholds for excitations of rotational states.

the molecule toward the electron when $B_r = 0$. If this migration causes some pole to be close to the positive real semiaxis of the physical sheet, it yields a resonance contribution to the scattering.

What we have said is illustrated by Figs. 12 and 13, which show the sum of the eigenphases for scattering by the LiF and HF molecules. When $J = 0$, the behavior of δ_{sum} for LiF arises from a bound state with the energy 0.235×10^{-5} eV. We can conclude from this that the LiF$^-$ ion has three $^2\Sigma^+$ states with binding energies of the electron of 0.33, 0.495×10^{-2}, and 0.235×10^{-5} eV. When $J = 1$ and $J = 2$, relatively broad shape resonances occur. For HF, three groups of curves are given that correspond to different values of α, since a sufficiently exact value of the electron-affinity energy in the Born-Oppenheimer approximation is not known. In the case $J = 0$ with $\mathscr{E}^{ad} = 10^{-5}$ and 10^{-4} eV, one
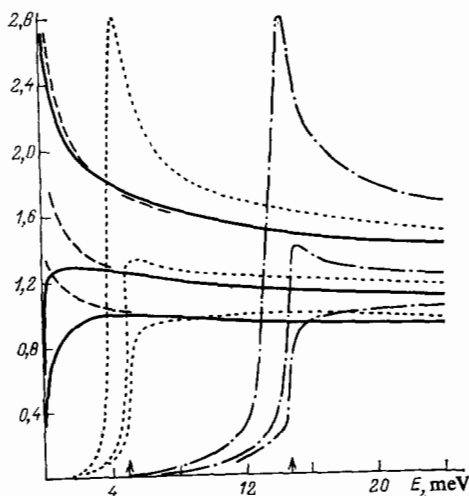

FIG. 13. Sums of eigenphases (apart from a term $N\pi$) for scattering by the HF molecule. Solid curve—$J = 0$; dots—$J = 1$; dot-dash—$J = 2$; dotted lines—adiabatic approximation, $J = 0$. For each J the lower curve corresponds to the case $\mathscr{E}^{ad} = 10^{-5}$ eV, the middle curve to the case $\mathscr{E}^{ad} = 10^{-4}$ eV, and the upper curve to the case $\mathscr{E}^{ad} = 10^{-3}$ eV. The arrows indicate the thresholds for excitation of rotational states.

observes scattering by a virtual state with energies 0.38×10^{-3} and 0.14×10^{-4} eV. When $\mathscr{E}^{ad} = 10^{-3}$ eV, the Crawford-Garrett criterion is fulfilled, and a bound state exists with an energy of 0.56×10^{-3} eV. In the cases $J = 1$ and $J = 2$, shape resonances exist, which are sharpest when $\mathscr{E}^{ad} = 10^{-3}$ eV.

The studied resonances have a width of the order of 0.1 B_r. Hence they cannot be observed in scattering experiments with the existing experimental technique. However, one can observe them in photodetachment experiments, owing to the large resolving power of the laser. Experiments of this type have already been perfomed for the negative ions of the sodium halides[124] and the ions of organic molecules.[125] In the latter experiment resonances were observed that apparently are of dipole type.

4. VIBRATIONAL EXCITATION

We can naturally divide the processes of collision of electrons with molecules that alter the vibrational state into two classes: nonresonance and resonance. To describe the former the impulse approximation usually suffices (e.g., this approach has been applied in Ref. 126); analysis of the latter presents great difficulties. From the physical standpoint, one can represent resonance processes as occurring in three stages: in the first stage the incident electron is captured by the electron shelll of the molecule and forms the state of an intermediate molecular ion. In the second stage the nuclei move in the field of the electron shell of this ion, while the decay of the ion in the course of this motion constitutes the third stage of the process. This qualitative picture enables one directly to reveal the role of the potential curve $W_I(R)$ of the molecular ion and the amplitudes for capture and detachment of the electron $V(R)$ in the description of the resonance processes. We note that the analysis of the fundamental time parameters of the process shows that, although the lifetime of the intermediate state in the case of sharply marked resonances exceeds the period of vibration of the nuclei, nevertheless it proves to be considerably smaller than the rotational period. Therefore we can consider the direction of the internuclear axis to be fixed in the course of the collision.

The best-known example of an intermediate resonance is the $^2\Pi_g$ state of the N_2^-. We have mentioned this resonance in Sec. 2b,1. The first ab initio calculation of this state was performed in Ref. 127. The results obtained in Ref. 127 are of great qualitative interest, and hence we shall take them up in somewhat greater detail. The calculation of the $^2\Pi_g$ resonance was performed within the framework of the self-consistent-field method, and the test functions were composed of Gaussian packets. When the width of these packets were restricted within limits of 5 Å, a local minimum was found of the variational functional at a function with the symmetry $^2\Pi_g$ (N_2^-): $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g$. Comparison of the $1\pi_g$ orbital of this state with the $1\pi_g$ orbital of the excited state of the N_2 molecule $(^1\Pi_g)$: $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_g^4 3\sigma_g 1\pi_g$ showed that, when $r \leqslant 2$ Å (r is the radial coordinate of the electron), these orbitals are similar, while when 2 Å $< r < 4$ Å, the orbital of the ion has an addi-

tional maximum interpreted as a manifestation of the decay of the state. An attempt to find a resonance associated with other excitations of the molecule, e.g., the $^1\Sigma_u^+$ state $(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g 3\sigma_u)$, failed. We can conclude from this study that the localization of the electron in the resonance state involves the existence of a centrifugal barrier for the smallest orbital angular momentum l_{min} allowed by the symmetry of the resonance (for the $1\pi_g$ orbital $l_{min} = 2$, and for the $3\sigma_u$ orbital $l_{min} = 1$). If the vacant orbital is localized inside this barrier, it can give rise to an intermediate resonance in electron scattering, whereas Rydberg states of the molecule localized solely by the Coulomb field and concentrated outside the centrifugal barrier, as, e.g., the $3\sigma_u$ orbital of the N_2 molecule, cannot give rise to such a resonance.

The mechanism of formation of a resonance described above, which is called a shape resonance in the literature, is not the sole mechanism. Resonances also exist (at larger energies of the electron) involving excitation of one of the electrons of the shell of the molecule (similarly to doubly excited states of atoms), and called in the literature Feshbach resonances.

Ab initio calculation of the parameters of intermediate resonances with fixed nuclei is the topic of a large number of studies, which constitute an entire field in modern computational quantum physics. We can crudely classify the calculations into "collisional," employing the integration of systems of strong-coupling equations,[1,136,137] and the method of the R-matrix, which was developed in Refs. 128–135. A number of problems arises when one uses the method of strong coupling of channels, involving allowance for exchange and dynamic polarization interaction. Therefore the method of the R-matrix currently seems more promising. With this we shall close the discussion of calculations in the fixed-nuclei approximation, and shall consider all the characteristics of the system in this approximation to be known.

An attempt to calculate the dynamics of motion of the nuclei "from first principles" has been undertaken in a series of studies.[138–140] However, this attempt, which rests on expanding the wave function of the system in the vibrational functions of the molecule, proved hardly successful. The reason for failure has been pointed out by Schneider[141]: the motion of the nuclei in the molecular ion is determined by the potential curve $W_1(R)$, which substantially differs from the potential curve $U_0(R)$ of the molecule. Naturally, a correct description of this motion requires a large basis of vibrational functions of the molecule. A calculation by using the method of the R-matrix, including in the treatment the motion of the nuclei,[10,142] has proved considerably more successful among the calculations "from first principles." On the whole, *ab initio* calculations are rather complex, and a semiphenomenological approach is widely applied in the current literature that rests on the theories of Bardsley and Herzenberg. We shall proceed to the description of the latter.

a) The theory of Bardsley

The most complete theory of resonance collisions of electrons with diatomic systems is the theory proposed by Bardsley[11]; a similar approach has been developed also in Refs. 143–145. In essence the theory of Bardsley is a natural generalization of the resonance theory of Feshbach and Fano[146,147] that allows one to take into account the quantum motion of the nuclei. Let us describe briefly Bardsley's approach, while mainly having in mind the introduction of the notation.

First of all we note that Bardsley's theory is most suited for studying Feshbach resonances. Such a resonance is described by the vector $|res; q,R\rangle$ (q is the set of electronic coordinates, and R of the unclear coordinates), which one can construct in the usual way from orbitals (occupied and vacant) of the molecule. This state is quadratically integrable, and we shall consider it to be normalized to unity with respect to the electronic coordinates. The state $|res\rangle$ is mixed with the scattering states of the electron by the molecule having an unexcited electron shell $|k,q,R\rangle$, as characterized by the momentum k of the incident electron. These states can be constructed by solving the problem of scattering of the electron by the molecule with fixed nuclei. We can assume that the states $|res\rangle$ and $|k\rangle$ are orthogonal in the electronic coordinates and depend weakly on R. We can take into account the mixing of these states by seeking the eigenfunction of the Hamiltonian $\hat{H} = \hat{T}_N(R) + \hat{H}_{el}(q,R)$ ($\hat{T}_N$ is the operator for the kinetic energy of the nuclei, and $\hat{H}_{el}$ is the Hamiltonian in the fixed-nuclei approximation) corresponding to the eigenvalue E in the following form:

$$|\Psi(R)\rangle = \xi(R)|res\rangle + \sum_n \int dk\, b_n(k)\, \varphi_n(R)|k\rangle. \quad (4.1)$$

(Here φ_n is the wave function of the nuclei in the state n having the energy E_n.) The coefficient functions $\xi(R)$ and $b_n(k)$ are determined by the variation principle. As a result one obtains the following equation for the function $\xi(R)$:

$$\left[-\frac{1}{2M}\frac{d^2}{dR^2} + U_0(R) - E \right]\xi(R) = -\varphi_{n_0}(R)\,V(k_0,\ R)$$

$$- \sum_n \varphi_n(R) \int \frac{dk}{E - E_n - E(k) + i0}\, V^*(k,\ R)$$

$$\times \int dR'\, V(k,\ R')\, \varphi_n(R')\, \xi(R'). \quad (4.2)$$

Here M is the reduced mass of the nuclei, n_0 is the initial vibrational state, k_0 is the momentum of the incident electron, and $E(k)$ is the energy of the state k. The energy of the resonance state $E_d(R)$ is defined as the mean value of the electronic Hamiltonian in this state. The quantity $V(k\,R)$ has the meaning of the capture amplitude of the electron:

$$V(k,\ R) = \langle res;\ q,\ R|\hat{H}_{el}(q,\ R)|k;\ q,\ R\rangle. \quad (4.3)$$

We must point out that the derivation of (4.2) presupposes using the adiabatic rule of differentiating with respect to R'', in which the dependence on R of the states $|res\rangle$ and $|k\rangle$ is not differentiated.

One can find the coefficients $b_n(k)$ and calculate the transition cross-section for $n_0, k_0 \to n, k$ from the known function $\xi(R)$:

$$\frac{d\sigma}{d\Omega_k} = \frac{16\pi^4}{k_0^2}\left|\int dR\, \xi(R)\, V(k,\ R)\, \varphi_n(R)\right|^2. \quad (4.4)$$

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(Here **k** is the momentum of the electron in the final channel.) Thus a calculation of the cross-sections for vibrational transitions within the framework of Bardsley's theory requires that we know the functions $E_d(R)$ and $V(\mathbf{k}, R)$. Yet one can find these functions only by using calculations that lie at the limit of contemporary computational potential.

b) The theory of Herzenberg

In contrast to the theory of Bardsley, the theory of Herzenberg, which was first proposed in Ref. 12 and is known as the "boomerang model," is more adapted to describing shape resonances. Herzenberg's approach has been developed in Refs. 149 and 151, and the most refined form of the theory is presented in Ref. 152.

In Herzenberg's theory one assumes that the wave function of the incident electron near the molecule is proportional to a quasistationary state function having the complex energy $W_1 - U_0$ (U_0 is the potential energy of the molecule), while at large distances this function is represented by the sum of the incident and outgoing electron waves. The motion of the nuclei in the resonance state is described by the wave function $\xi(R)$, which satisfies the equation

$$\left[-\frac{1}{2M} \frac{d^2}{dR^2_f} + (W_1(R) - E) \right] \xi(R) = -V(R)\, \varphi_{n_0}(R). \quad (4.5)$$

(Here V is the capture amplitude of the electron.) The cross-section of the transition $n_0 \to n$ is calculated from the function $\xi(R)$ just as in the theory of Bardsley [see (4.4)].

The cross-sections for vibrational excitation have been calculated by using Herzenberg's theory for a number of molecules: N_2,[12,149,151,152] CO,[153,154] N_2O,[158] and CO_2.[155–157] In these calculations the energy curves of the ion and the molecule were parametrized by using Morse potentials. The width Γ of the intermediate state was determined from the penetrability of the centrifugal barrier having the lowest orbital angular momentum admissible by the symmetry of the resonance (in this connection we shall be speaking below of l-dominance). The amplitude of electron capture $V(R)$ is determined in Herzenberg's theory from the width $\Gamma(R)$ by using the optical theorem.[52]

Despite the crudeness and not always sufficient justification of the representations of $\Gamma(R)$ and $V(R)$, it was possible in the above-cited studies to obtain very good qualitative agreement with experiment by adjusting the parameters (within reasonable bounds). It remains not fully clear whether one must seek a refinement of the representations of $\Gamma(R)$ and $V(R)$, or whether such refinements will exceed the accuracy of the Herzenberg theory itself.

It is important to note that Herzenberg's theory enables one to determine also the differential cross-section for vibrational excitation[151]:

$$\frac{d\sigma_{n_0 \to n}}{d\Omega} = \sigma_{n_0 \to n} g(\vartheta).$$

Here, e.g., in the case of the $^2\Pi_g$ resonance of the N_2 molecule, we have

$$g(\vartheta) = \frac{1}{4\pi} \frac{15}{14} \left(1 - 3\cos^2\vartheta + \frac{14}{3}\cos^4\vartheta \right). \quad (4.6)$$

Here ϑ is the scattering angle (the representation (4.6) has been discussed in a number of studies).

Equation (4.6) is based only on the assumption of l-dominance and matches the experimental results well. Traces of l-dominance can be found also in studying inelastic vibrational-rotational transitions.[1] The theory of such processes resembles the hybrid theory developed here: vibrational excitation can be described within the framework of the Herzenberg theory, and rotational transitions studied by using the impulse approximation. We note that such an analysis is difficult for super-longlived resonances (e.g., the O_2^- molecular ion), for which the lifetime of the intermediate state is comparable with the period of rotation of the molecule.[150]

c) Comparison of the theories of Bardsley and Herzenberg

The problem of the relation between the theories of Herzenberg and Bardsley has not been finally elucidated. It is usually stated,[100] following Bardsley's founding study,[11] that the integral equation of Bardsley becomes local at large values of the energy E of the system. However, this is not the sole argument. Let us turn attention to three aspects of the topic under discussion.

First, both theories are approximate. Hence the problem is correctly posed as: does the difference between the results of calculations within the framework of these theories exceed the accuracy of the theories themselves. There is as yet no answer to this question.

Second, in the limit of infinitely heavy nuclei, when their motion ceases to play a role, the state used in the theory of Bardsley mixes with the continuum, acquires a width, and goes over into the quasistationary state of Herzenberg's theory. Therefore we can naturally expect that both theories will give similar results in the quasiclassical limit. This problem has been discussed in part in Ref. 211, but there is as yet no detailed analysis.

Third, we should not forget in comparing the theories that they describe somewhat differing physical situations—one of them is adapted to describing Feshbach resonances, and the other to describing shape resonances. The question remains open in comparing the theories of the error associated with this circumstance.

d) Quasiclassical approximation

The attempts at an analytical solution of the equation of Herzenberg (4.5) and calculation of the cross-sections in (4.4) undertaken in Refs. 180, 184, and 160 are of interest. The former studies will be discussed below. Reference 160 employed a representation of the energy curves of the molecule U_0 and the ion U_1 using Morse potentials, while the width of the intermediate state was taken into account within the framework of perturbation theory. Representations for the cross-sections were obtained in the form of multiple series; use of these representations enabled a good match of the "high-energy" region of the experimental curves.

As we have already mentioned, in deriving the fundamental equations of the theories of Bardsley and Herzenberg, one applies the rule of "adiabatic differentiation," which is based on the fact that the mass of the nuclei is larger than the mass of an electron. It is of interest to try to use this

fact also in constructing solutions of these equations consisting in representing the cross-sections by the principal term of their asymptotic expansions in tems of the appropriate large parameter. Such a representation, as constructed within the framework of Herzenberg's theory,[161-163] made it possible to obtain compact and pictorial formulas for the cross-sections that generalize in a natural fashion the generally accepted assumptions associated with the Franck-Condon principle. The numerical calculations performed in Refs. 161-163 showed that the quasiclassical formulas yield a good approximation, both to the known experimental data and to the results of exact integration of Herzenberg's equations, even when the formal conditions for applicability of the quasiclassical approximation are violated.

The quasiclassical representation of the cross-sections for the vibrational transition have the following form:

$$\sigma_{n_0 \to n} = \frac{k_n}{k_{n_0}} \frac{1}{8\pi^3} \frac{|I_n|^2 |I_{n_0}|^2}{|Q|^2}. \qquad (4.6')$$

Here we have

$$Q = \sin \left(\int_{a_{\mathrm{I}}}^{b_{\mathrm{I}}} p_{\mathrm{I}}(z)\, dz - \frac{\pi}{4} \right), \quad p_{\mathrm{I}}(z) = \sqrt{2M\,[E - W_{\mathrm{I}}(z)]}.$$

Further, a_{I} and b_{I} are the turning points for a molecular ion having the energy E (generally these points are complex), while the quantities I_{n_0} and I have the form of Franck-Condon factors, and are determined by the behavior of the wave functions in the neighborhoods of the transition points R_{n_0} and R_n, which satisfy the generalized Franck-Condon principle

$$E - W_{\mathrm{I}}(R_k) = E_k - U_0(R_k), \quad k = n,\ n_0.$$

Here E_k is the energy of the k th vibrational state. Equation (4.6') has a considerable heuristic value is confirming the division of the process of vibrational excitation into three states. Thus, the factor $|I_{n_0}|^2$ does not depend on n, and amounts to the probability of capture of the incident electron

into the resonance state, whereas $|I_n|^2$ is the probability of decay of this state. The role of the denominator $|Q|^2$ is especially large when the width Γ is small. Then, at energies close to the roots of the equation

$$\int_{a_{\mathrm{I}}}^{b_{\mathrm{I}}} p_{\mathrm{I}}(z)\, dz = \pi \left(n + \frac{1}{2} \right),$$

which determines the quasiclassical levels of the molecular ion, the cross-sections have sharp Breit-Wigner maxima. As the width of the term increases, these resonance maxima broaden, and in the case of the N_2, CO, and CO_2 molecules, the denominator $|Q|^2$ ceases to play the determining role in the energy-dependence of the cross-sections. For these molecules, the stated dependence is determined by the interplay of the factors $|I_{n_0}|^2$ and $|I_n|^2$. Here the former factor is responsible for the "low-frequency" part of this dependence, while $|I_n|^2$ determines the "high-frequency" oscillations (Fig. 14).

Numerical calculations performed within the framework of the quasiclassical approximation yielded results agreeing well with the data of Ref. 152 for the N_2 molecule (Fig. 15). In the case of the CO molecule, the quasiclassical calculation matches the results of Refs. 153 and 154 only qualitatively, while the absolute values of the cross-sections differ by a factor of about two. However, we must point out that in Refs. 153 and 154 the absolute values were determined by fitting to the experimental data.[165] As was pointed out in Ref. 166, the latter have an accuracy comparable with the deviation between the data of Refs. 153 and 154 and experiment.[163] The latest data on this process (total cross-section) were obtained quite recently,[216] and the measured resonance cross-section exceeds the data of Ref. 153 by a factor of about 1.5. Thus, the discrepancy between the results of Refs. 153, 154 and Ref. 163 cannot be grounds for mistrusting the quasiclassical method.
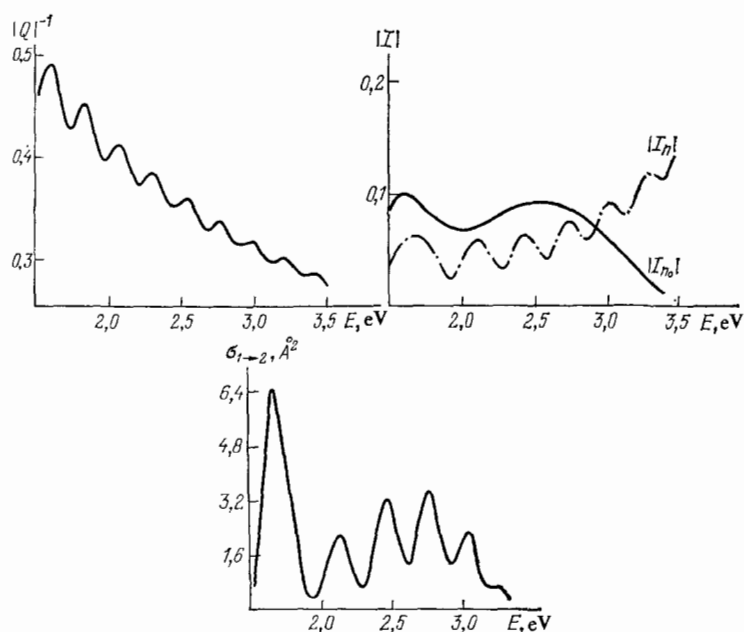

FIG. 14. Dependence of the factors entering into Eq. (4.6') on the energy of the incident electron for the $n_0 = 1 \to n = 2$ transition in the N_2 molecule.
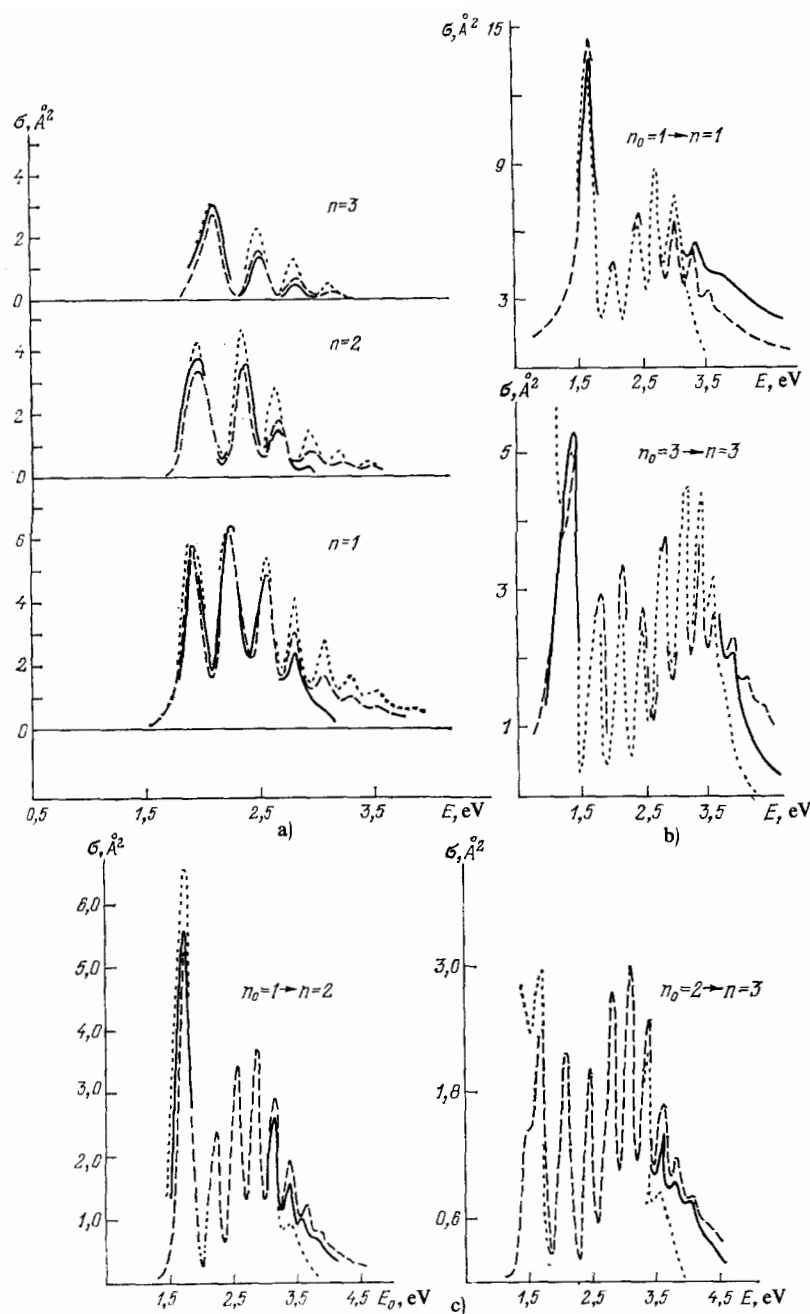
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FIG. 15. Cross-sections of vibrational transitions in the N_2 molecule. a) Vibrational excitation from the ground state: dots—experimental data[164]; solid curve—quasiclassical calculation; dotted curve—calculation of Ref. 152; b) cross-sections for resonance elastic scattering: dots—quasiclassical calculation by Eq. (4.6'); solid curve—quasiclassical calculation by the improved formulas[163]; dotted curve—calculation of Ref. 152; c) cross-sections of vibrational transitions between excited states; the coding of the curves is the same as in b).

e) Dissociative recombination

The dissociative recombination

$$(AB)_{n_0} + e^- \rightarrow A + B^-$$
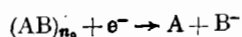
is a process related to vibrational excitation. While competing with the latter, it occurs at energies of the system exceeding the threshold value E_{th} (Fig. 16). In this case the intermediate state formed after capture of the electron can either decay into the final vibrational state by losing the electron or can "survive" to the point $R = R_{stab}$ that separates the region of instability of the intermediate system from its region of stability. In the latter case the electron is localized on one of the atoms in the course of the further separation of the nuclei. The described pattern allows one to apply methods to describe the process that were developed to study vibrational excitation. Thus, the motion of the nuclei in the intermediate state is characterized by the wave function $\xi(R)$, which satisfies either Eq. (4.2) or Eq. (4.5), depending on the model adopted to describe the process, together with the boundary condition as $R \rightarrow \infty$:

$$\frac{d\xi}{dR} \sim i \sqrt{2M [E - W_I(R)]}\, \xi. \tag{4.7}$$

The cross-section for vibrational transitions is determined as before by (4.4), while the cross-section for *dissociative recombination* (DR) must be calculated from the flux of the function $\xi(R)$ at large internuclear distances:

$$\sigma_{n_0}^{DR} = - i\, [8\pi M \sqrt{2(E - E_{n_0})}]^{-1} \left(\xi^* \frac{d\xi}{dR} - \xi \frac{d\xi^*}{dR} \right) \Big|_{R \rightarrow \infty}. \tag{4.8}$$
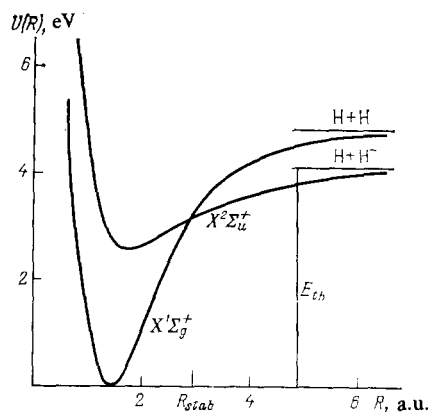
FIG. 16. Energy curves of the lower states of the hydrogen molecule and the corresponding molecular ion. The curves have been employed in Refs. 168 and 169 to calculate the process of dissociative recombination.

The formulation of the problem has been known for a long time,[170,171,211] but until recently no quantitative calculations of the process had been performed. (We must note a new approach to the process developed in Refs. 172–175 and based on the methods developed to study the three-body problem.) Recently, in connection with the growing experimental interest in DR, calculations have appeared for the molecules F_2,[148,167] and H_2, HD, and D_2.[168,169] The most "powerful" calculation of DR–in the F_2 molecule–was perfomed in Ref. 148 by using the nonlocal approach of Bardsley [Eq. (4.2)] to describe the dynamics of the nuclei. Here the wave function of the intermediate state was calculated *ab initio*. This precision calculation reproduces the experimental data only qualitatively, whereas the semiempirical calculation[167] based on the local approach of Herzenberg (4.5) enables one to obtain results agreeing well with the experimental data. We note that there is a qualitative difference between the results of Refs. 148 and 167 at low electron energies, which has been discussed in Ref. 148. We must bear in mind the fact that neither theory nor experiment are reliable enough in this region.

The DR calculation for the H_2, HD, and D_2 molecules perfomed in Refs. 168 and 169 is semiempirical and is based on a local variant of the resonance theory (4.5). The potential curves of the system are shown in Fig. 16. The calculation[168,169] took into account both the two final channels of the reaction ($x^1\Sigma_g^+$ and $b^3\Sigma_u^+$) and the two intermediate states of the molecular ion $X^2\Sigma_u^+$ and $B^2\Sigma_g^+$. We should note that the results obtained in these studies do not agree sufficiently well with experiment. This indicates an insufficient accuracy, and to a certain extent contradictory quality, of the experimental data; this problem has been discussed in detail in Ref. 169.

It is of interest to apply the methods developed for vibrational excitation and based on the quasiclassical approximation to describe DR processes. Such a description has been discussed earlier and all the fundamental formulas derived.[170] The quasiclassical approach made it possible to draw a number of useful conclusions, especially with regard to the isotopic dependence of the cross-sections,[171] which have been confirmed experimentally.[176] However, numeri-

cal calculations of DR had not previously been performed within the framework of the quasiclassical approximation (the calculation performed in Ref. 177 started with a classical description of the motion of the nuclei and hence is insufficiently exact). Let us give the fundamental formula for the DR cross-section in the quasiclassical approximation:

$$\sigma_{n_{\bullet}}^{DR} = (2\pi \sqrt{E - E_{n_0}})^{-1} M A^2 |I_{n_0}|^2, \qquad (4.9)$$

Here we have

$$A = \exp\left(-\mathrm{Im} \int_{a_{\mathrm{I}}}^{R_{\mathrm{stab}}} p_{\mathrm{I}}(z)\, dz\right).$$

As we have already said, the factor $|I_{n_0}|^2$ has the meaning of the probability of electron capture, while the factor A can be naturally called the survival factor of the system in the intermediate state to the point R_{stab}. For hydrogen molecules, the width $\Gamma(R)$ of the term of this state proves to be large and enables one to transform Eq. (4.9):

$$\sigma_{n_0}^{DR} = \frac{\omega\, |V(R_{n_0})|^2}{4\pi} \sqrt{\frac{M}{(E-E_{n_0})(E-W_{\mathrm{I}}(R_{n_0}))}}$$

$$\times \left(\frac{dU_0}{dR} - \frac{dU_{\mathrm{I}}}{dR}\right)\Big|_{R=R_{n_0}}$$

$$\times S \exp\left(-2\,\mathrm{Im} \int_{a_{n_0}}^{R_{n_0}} \sqrt{2M[E_{n_0} - U_0(z)]}\, dz\right), \quad (4.10)$$

$$S = \exp\left(-2\,\mathrm{Im} \int_{R_{n_0}}^{R_{\mathrm{stab}}} p_{\mathrm{I}}(z)\, dz\right); \qquad (4.11)$$

Here a_{n_0} is the left-hand turning point for a molecule in the initial state. Physically this approximation is explained as follows. In line with the Franck-Condon principle, the capture of the electron occurs at the point R_{n_0}, while the intermediate system conserves the direction of motion of the nuclei. Naturally, only capture of the electron while the nuclei are separating leads in the case of a large width to DR. It is of interest to compare (4.11) with the classical representation (with respect to the motion of the nuclei) of the survival factor:

$$S_{\mathrm{cl}} = \exp\left[-\int_{R_a}^{R_{\mathrm{stab}}} \Gamma(R)\frac{dR}{v(R)}\right], \qquad v = \sqrt{\frac{2(E-U_1(R))}{M}} \qquad (4.12)$$

(In this formula, which can be used for describing the process of recombination with the ground vibrational state of the molecule, R_0 is the equilibrium distance between the nuclei.) Correspondence between (4.11) and (4.12) is established by expanding $\mathrm{Im}\int_{R_{n_0}}^{R_{\mathrm{stab}}} p_1(z)\, dz$ in (4.11) as a series for small Γ. One can say that the difference between (4.11) and (4.12) is substantial when the width is large.

Reference 178, which we discussed above, quantitatively compared (4.10) with the results of integrating Eq. (4.5) (Fig. 17). It is of interest to study the isotopic dependence of the DR cross-section—a problem that has become traditional following Ref. 171. It was shown[178] that, in line with (4.10), the quantity
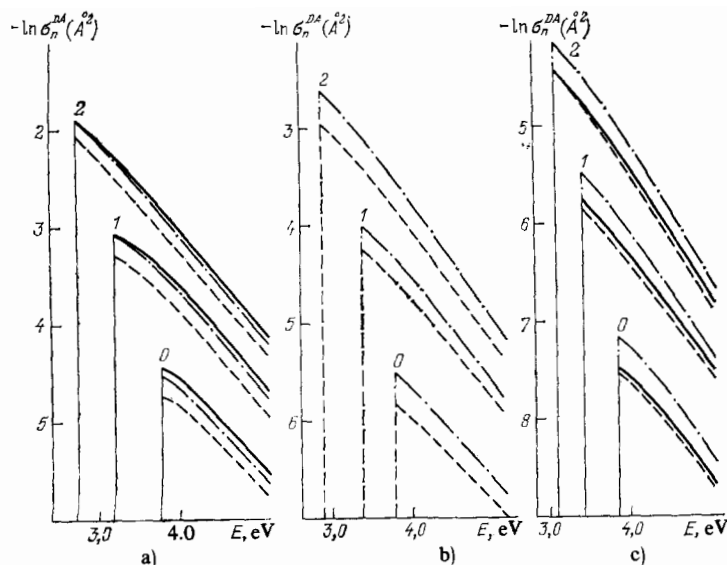
FIG. 17. Cross-sections for dissociative recombination for the molecules H_2 (a), HD (b), and D_2 (c) as functions of the energy of the incident electron. Solid curves—calculation of Ref. 168 for Fig. a), and of Ref. 169 for Fig. b); dot-dash curves—quasiclassical calculation with the parameters of Ref. 168; dotted curves—quasiclassical calculation with the parameters of Ref. 169 (we should note that Refs. 168 and 169 employed slightly different representations of the width of the intermediate state).

$$q = \frac{\ln(\sigma_{H_2}/\sigma_{HD})}{\ln(\sigma_{H_2}/\sigma_{D_2})}$$

is close to the classical value $q_0 = (2-\sqrt{3})/(\sqrt{6}-\sqrt{3}) \approx 0.374$. Experiment yields $q \approx 0.38$.

f) Exactly solvable models in the theory of vibrational excitation

Exactly solvable models occupy a special position in developing the theory of various physical phenomena. To avoid confusion, let us point out immediately that the exact solvability of a model does not presuppose the existence of an analytic solution expressing the physical quantities in terms of known special functions; it is quite sufficient to have a computer algorithm that enables one to perform calculations of any characteristics of the system. As an example explaining this statement, let us present the problem of two Coulomb centers.[179]

On the other hand, exactly solvable models enable one to test different physical hypotheses, and on the other hand, they make it possible to find hidden features of the processes and help in forming new concepts and pictures. Therefore such models must, first, be sufficiently specific (in order to be solvable), and second, yield a broad enough region of variation of the parameters (in order to yield a representation full of content for the processes being studied). In a number of cases, exactly solvable models developed to solve certain problems have proved useful also in other fields of physics. Therefore we hope that the models given below are of a certain general physical interest.

1) The model of Domcke and Cederbaum

The model to be discussed in this section was first proposed in Ref. 180 and subsequently discussed in a series of papers.[181-183] The first publication employed the field-theoretical language of second quantization, which is not necessary in the given problem, as we see it. We shall formulate the model in the language more natural in the given case of the Feshbach-Fano theory.

We treat the interaction of the discrete electronic state $|d\rangle$ and the electron continuum $|k\rangle$ ($\langle d|d\rangle = 1$, $\langle k|k'\rangle = \delta(k-k')$, $\langle d|k\rangle = 0$; all the states are independent of the internuclear distance R) that are described by the Hamiltonian

$$\hat{H}^{DC} = -\frac{1}{2M}\frac{d^2}{dR^2} + U_0(R) + v(R)|d\rangle\langle d|$$

$$+ \int_0^\infty dk\, w(k)|k\rangle\langle k| + \int\int_0^\infty dk\,dk'\, w_1(k,k')|k\rangle\langle k'|$$

$$+ \int_0^\infty dk\, (V_d(k,R)|d\rangle\langle k| + V_d^*(k,R)|k\rangle\langle d|). \quad (4.13)$$

Here $w(k)$ has the meaning of the state energy of the continuum, $w(0) = 0$, $w > 0$ when $k > 0$; $U_0(R)$ amounts to the potential energy of the molecule for the Hamiltonian of (4.13); U_0 is the lower bound of the electron continuum. One can eliminate the interaction among the states of the continuum w_1 by diagonalizing the Hamiltonian in the space of continuum states. Hence we shall assume below that $w_1(k,k') = 0$. Within the framework of the model being discussed, one can obtain formally exact representations for the transition amplitudes between the initial state n_0, k_0 and the final state n, k, $A_{n_0,n}$, but one can use these representations to obtain numerical results only in certain special cases. The reason for this is that the given model is an exactly solvable formulation of the theory of Bardsley, and hence is not specific enough.

In order to elucidate the physical meaning of the model, we should examine the limit for fixed nuclei. The position of the resonance level in this approximation is determined from the equation

$$E = U_0(R) + v(R) + \Delta(E - U_0(R), R)$$

$$- \frac{i}{2}\Gamma(E - U_0(R), R). \quad (4.14)$$

Here we have

$$\Gamma(E,R) = 2\pi\int dk\, \delta(E - w(k))|V_d(k,R)|^2, \quad (4.15)$$

$$\Delta(E,R) = \frac{1}{2\pi} \text{ V. P. } \int \frac{dE' \, \Gamma(E',R)}{E-E'} . \qquad (4.16)$$

Equation (4.14) often (especially in the presence of long-range interaction) proves to be nontrivial, and its solution has been discussed in Refs. 182 and 183.

On returning to the expression for the amplitudes $A_{n_0,n}$, let us discuss the possibility of informally calculating it. Two cases are known in which such a calculation is possible.

1. $V_d(k,R)$ does not depend on $R, U_0(R) = M\omega^2 R^2/2$, $\Delta(E,R) - i\Gamma(E,R)/2 = \gamma R + \delta$. In this case a closed expression has been obtained[180] for the amplitude in the form of a single series in Laguerre polynomials. We must say that this result has been derived by a more elegant method in Ref. 184.

2. $V_d(k,R)$, $\Delta(E,R)$, and $\Gamma(E,R)$ do not depend on R. It is assumed that the $\Gamma(E)$ relationship is determined by the threshold law, while the $\Delta(E)$ relationship is found from $\Gamma(E)$ by using (4.16); $U_0 = M\omega^2 R^2/2$, and $v(R) = v_0 + kR$. In this case, in order to determine the transition amplitude, one must solve the three-term recursion relationships.[181-183]

Let us list the fundamental results obtained by studying the models being discussed.

1) It was shown in Ref. 180, just as in Ref. 184, that under the conditions 1 one can qualitatively reproduce the energy-dependence of the cross-sections for vibrational excitation of the nitrogen molecule. The lack of anharmonicity, the insufficiently realistic picture of the dependence of the width of the resonance on R, and the coincidence of the frequencies of the molecule and the ion did not allow a quantitative match with experiment with sufficient accuracy.

2) It was shown[181] by using variant 2 that taking account of the nonadiabatic coupling of the motion of the electron and the nuclei leads to narrowing of the resonance maxima (for a small width of the resonance) as compared with the adiabatic Breit-Wigner formula.

3) In Refs. 182 and 183 variant 2 was applied for studying the effect of the long-range dipole interaction between the electron and the molecule on the viabrational excitation. They showed that taking account of the long-range interaction can substantially change the behavior of the cross-sections for vibrational excitation near the threshold. In principle it can lead to sharp threshold features, which have been found experimentally.[185-188] In addition to the dipole interaction, Refs. 182 and 183 have treated also the effect of an intermediate virtual state. However, the analysis in these studies, as we see it, is narrowly modeling in type, and hence it does not allow drawing conclusions associated with experiment.

2) The model of emergence of a term into the continuous spectrum

The concept of the emergence of a term of the intermediate state into the continuous spectrum as an adiabatic mechanism of detachment of an electron has been widely employed[56] in the theory of collisions of heavy particles at sufficiently high energies at which the description of the motion of the nuclei in terms of classical mechanics is applicable. A more complete theory of such processes is the model of Demkov and Osherov.[189-194] This model allows general-

ization to the case of quantum motion of the nuclei in the absence of interaction between them,[190,192,194] and a concrete special case of this problem has been treated in Ref. 195. However, in collision of electrons with molecules, one must take into account the interaction of the nuclei[196]; the case in which this interaction is characterized by a constant force has been treated in Ref. 197. A more important representation of this interaction is the case of a harmonic potential, which has been studied in a series of papers.[198-203] We shall study specifically this model here, taking up in detail the physical assumptions of the model and the results obtained, and omitting the details of the mathematical solution of the problem.

Let us examine a system described by the Hamiltonian

$$\hat{H} = -\frac{1}{2M} \frac{d^2}{dR^2} + \frac{M\omega^2 R^2}{2}$$
$$-\frac{1}{2}\frac{\partial^2}{\partial r^2} + V(r) + (\beta R + U)|\varphi\rangle\langle\varphi|. \qquad (4.17)$$

Here the internuclear distance R is measured from the equilibrium position of the molecule. Hence it is convenient to assume that $R \in (-\infty,\infty)$, while the radial coordinate of the electron $r \in [0,\infty)$, $V(r)$, characterizes the long-range interaction of the electron with the molecule, and their short-range interaction is described by a separable potential. The Hamiltonian (4.17) is a natural generalization of the Demkov-Osherov potential.[56,189-194]

In the fixed-nuclei limit, the Hamiltonian (4.17) has a continuous spectrum in the electron coordinate, with the minimum eigenvalue of the Hamiltonian (corresponding to zero momentum of the electron) equal to $M\omega^2 R^2/2$, and the discrete state is

$$|d(R)\rangle = \hat{G}^+(\varepsilon(R))|\varphi\rangle,$$

$$\hat{G}^+(\varepsilon) = \left(-\frac{1}{2}\frac{\partial^2}{\partial r^2} + V(r) - \varepsilon + i0\right)^{-1}. \qquad (4.18)$$

Its energy $T(R)$ is determined from the equation

$$T(R) = \frac{M\omega^2 R^2}{2} + \varepsilon(R),$$

where we have

$$\langle\varphi|\hat{G}^+(\varepsilon(R))|\varphi\rangle^{-1} = -(\beta R + U). \qquad (4.19)$$

Evidently, when $\beta < 0$, $\varepsilon(R)$ increases to zero with decreasing R, and then becomes complex—the term $T(R)$ crosses the boundary $M\omega^2 R^2/2$ of the continuous spectrum and emerges into the continuum.

A simpler case is that with $V(r) = 0$, $\varphi(r) = \delta(r)$, which has been treated in Refs. 199-201. In this case we have

$$T(R) = \frac{M\omega^2 R^2}{2} - \frac{(\beta R + U)^2}{2} .$$

We see that, when $|\beta| < \sqrt{M\omega^2}$, $T(R)$ increases without limit with increasing R (Fig. 18a), i.e., the intermediate molecular ion is vibrationally stable (as occurs in the case of the O_2 molecule). When $|\beta| > \sqrt{M\omega^2}$, $T(R) \to -\infty$ as $R \to \infty$ (Fig. 18b), and the vibrational instability of the ion is expressed in the possibility of the process of dissociative recombination.

A very important property of the model is that all its physical characteristics are expressed in terms of the function $R(\varepsilon)$, which is determined by Eq. (4.19). This function
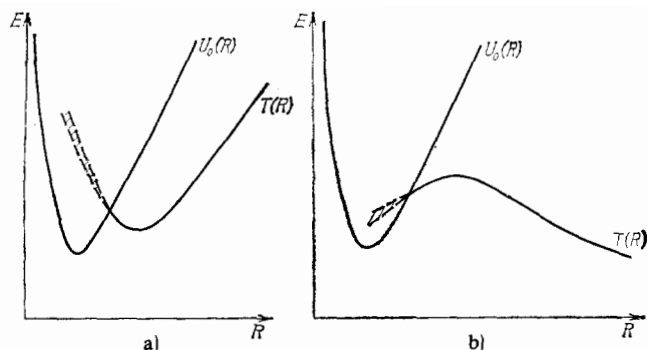
FIG. 18. Energy curves of the model of (4.17). a) The intermediate state is vibrationally stable; b) the intermediate state allows a channel of dissociative recombination.

can be called the Franck-Condon function, since when $\varepsilon > 0$, it determines the internuclear distance at which an electron with the energy ε is formed by decay of the intermediate state. Evidently, when $\varepsilon > 0$, we have Im $R(\varepsilon) > 0$, and when $\varepsilon < 0$, we have Im $R(\varepsilon) = 0$.

Another variant of the model of emergence of a term into the continuous spectrum has been discussed in Ref. 201, which treated a system having the Hamiltonian

$$\hat{H} = -\frac{1}{2M}\frac{\partial^2}{\partial R^2} + \frac{M\omega^2 R^2}{2} + \frac{J(J+1)}{2MR^2}$$
$$+ \hat{H}_0(r) + \beta(R^2 - R_0^2)|\varphi\rangle\langle\varphi|. \quad (4.20)$$

In contrast to (4.17), the boundary of the continuous spectrum for (4.20) is asymmetric, while the parameter J that characterizes this asymmetry does not necessarily involve the rotational motion of the nuclei, although the Hamiltonian of (4.20) allows one in principle to take account of this rotation. The quadratic nature of the dependence of the separable-interaction constant on R is not physically essential, since when $R\rightarrow 0$, the eigenfunction of (4.20) must fall off rapidly.

For the Hamiltonian of (4.17), we seek the solution of the problem for the eigenfunctions in the form of an expansion in Hermite functions, while for (4.20) this expansion is carried out in Laguerre functions. One uses the three-term recursion relations to determine the coefficients of these expansions.[199-201]

Let us proceed to describe the results obtained within the framework of these models. We note as a preliminary that the value of exactly solvable models is not determined by obtaining results close to the experimental—for this the models may prove to be too crude—but by the possibility of formulating a "mathematical experiment" that reveals the effect of varying the parameters of the system on its physical characteristics. Precisely from this standpoint should we treat the study of the role of the virtual intermediate state that has been adopted as the basis of the models being discussed.

A virtual state is formed in potential-scattering problems when, as the depth of a potential well decreases, the energy of a level localized in it passes through zero. If a barrier is present, then the level goes over into a quasistationary state. If there is no barrier, then the level becomes virtual

(antibound[204]). We have already discussed an analogous phenomenon above in Sec. 3d in connection with the motion of the poles of the S-matrix upon varying the rotational constant. We can naturally assume that, if the symmetry of the orbital occupied by the incident electron allows the orbital angular momentum to be $l = 0$, then the intermediate state will be specifically virtual. Study of the effect of a virtual state on vibrational excitation by the method of Herzenberg (Sec. 4b) is apparently quite impossible, while study by the method of Bardsley (Sec. 4a) is difficult, since one must solve an integral equation in which the role of the nonlocal terms is decisive. In this connection the value rises sharply of studying exactly solvable models which involve no substantial difference between quasistationary and virtual intermediate states. The first such study was undertaken in Ref. 198. Although its authors speak of the role of the dipole interaction, in essence they studied the problem of a virtual intermediate state. The complete solution of the model (4.17) for $V = 0$ and $\varphi(r) = \delta(r)$ was obtained in Ref. 199. In this study calculations were performed on the probabilities of vibrational transitions, dissociative recombination, and associative detachment for a certain randomly chosen set of parameters of the model. During the calculations resonances were found in these probabilities involving vibrational states of the molecular ion (these resonances have subsequently also been found in Ref. 202, where they were called Feshbach resonances), as well as a resonance involving tunneling through an activation barrier. In Ref. 202 the Feshbach resonances were discussed in connection with the study of threshold features in the vibrational excitation of the HCl molecule. However, this treatment was qualitative in character, since the potential curve of the molecular ion in Ref. 202 increases with increasing R, whereas *ab initio* calculations have shown[205] that this curve very rapidly becomes practically horizontal. A calculation was performed in Ref. 203 of the probabilities of vibrational excitation of HF and HCl molecules that methodologically almost coincide with Ref. 199. The probabilities of occupation of different vibrational states of the molecules upon associative detachment were found[203] as functions of the energy. It is important to note that the parameters of the model were chosen on the basis of calculations of the terms of the system: Ref. 205 for HCl and Ref. 206 for HF. The comparison of the results of Ref. 203 with the experimental data on the distribution of energy over the vibrational states of the molecule as a function of the temperature[207] showed that the accuracy of the model is quite satisfactory (Fig. 19).

Within the framework of the model (4.17) with $V = 0$ and $\varphi = \delta(r)$, one cannot take correct account of the motion of the poles of the adiabatic S-matrix: this model has no virtual pole that moves upward with decreasing R along the negative imaginary axis in the k-plane ($k = \sqrt{\varepsilon}$) to meet the pole corresponding to the bound state. Actually, in meeting at the negative imaginary axis, these poles, *in separating* practically parallel to the real axis, form a "cross" characteristic of the theory of the S-matrix.[56,204] Evidently, if the point of merging of the poles is close to the real axis, then the intermediate state will be quasistationary in character *rather* than virtual. An attempt to take into account the effect of a
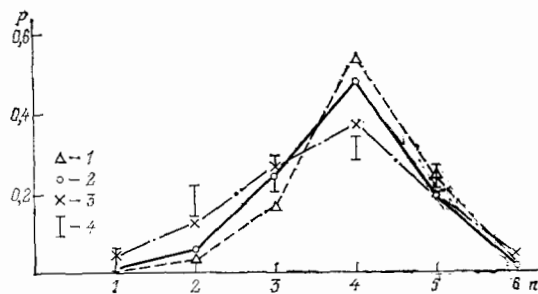
FIG. 19. Relative occupancy of the final vibrational states in $F^- + H$ collisions with a Maxwellian energy distribution. Cited from Ref. 203. 1—200 K; 2—300 K; 3—600 K; 4—experimental results,[207] $T = 300$ K.

second virtual pole on the processes being discussed has been undertaken in Ref. 201, where the following equation was chosen for determining the Franck-Condon function $R(\varepsilon)$:

$$(\sqrt{\varepsilon} + ik_0)^2 = -\alpha(R^2 - R_0^2).$$

(This is precisely the form of the coupling of ε and R in the case of the separable potential of Yamaguchi.[208]) Evidently ik_0 is the merger point of the roots of this equation in the k-plane. The parameter α determines the rate of motion of the poles with changing R, and R_0 is responsible for the position of the point R_{stab} of emergence of the term into the continuous spectrum: $R_{stab}^2 = R_0^2 + k_0^2/\alpha$. In the calculation of Ref. 202, the parameters of the model were chosen as follows: $J = 1$ and $\alpha = 0.58$ were taken arbitrarily, while the parameters k_0 and R_0 were varied in such a way as to fit the experimental data on vibrational excitation[185] and dissociative recombination[209] with the results of numerical calculation[205] of the energy curves for the HCl molecule. The agreement obtained could be described only as qualitative (Fig. 20), especially in connection with the considerable shift of the maximum in the cross-section of the 0→1 vibrational excitation from the threshold. Perhaps one must take into
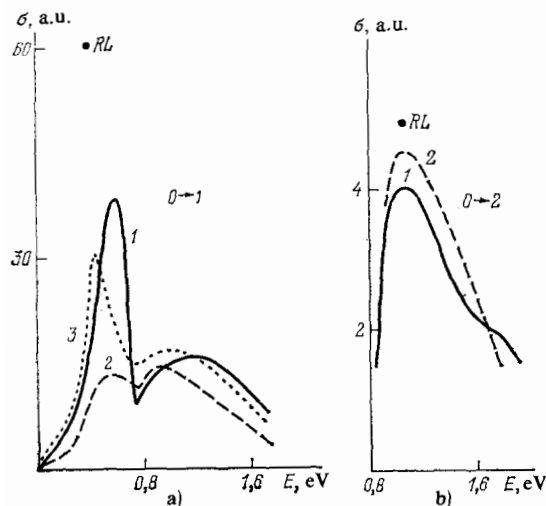

FIG. 20. Results of calculations of the processes of vibrational excitation and dissociative recombination for the HCl molecule. The calculations were performed[201] on the basis of the mode of (4.17) for three different values of the parameters of the model. The symbol RL indicates the position of the maxium of the cross-section observed experimentally.[185-188]

account the dipole interaction between the electron and the molecule to obtain the experimental results at the threshold.

g) Effect of dipole interaction and a virtual intermediate state on processes of vibrational excitation

The methods that we have treated appear to be useful in studying the relatively simple and general properties of the processes under discussion. As the most important for study, we note two problems associated with processes of vibrational excitation and dissociative recombination:

1. The effect on these processes of long-range dipole interaction.

2. The role of virtual intermediate states.

As experiments[185-188] have shown, both these problems are rather vital: both mechanisms have been discussed in connection with the HCl and HF molecules, while a virtual state is apparently responsible for the processes in the SF_6 and CH_4 molecules.

We must bear in mind the idea that the role of dipole interaction in the processes being discussed can be double.

First, the dipole interaction alters the threshold behavior of the S-matrix. This behavior near the threshold of the transition $n_0 = 0 \to n = 1$ is determined by the following formula[117] in the impulse approximation with respect to rotation, with a dipole moment $D > D_{cr}$:

$$S^{01} = \frac{ck_1^{i\mu}}{1 + k_1^{2i\mu} \exp(\pi\mu + i\alpha)}. \tag{4.22}$$

Here μ and α are the same parameters as enter into Eq. (2.12), while k_1 is the momentum of the departing electron, and c is a certain constant. Equation (4.22) shows that the energy-dependence of the cross-section near the threshold has an oscillating structure. However, this structure does not make a sharp resonance contribution: when $D_{cr} < D \lesssim 5D_{cr}$, μ is small, while the period of the oscillations is so great that two successive maxima do not lie simultaneously in the region of applicability of the theory, while when $D > 5D_{cr}$, the factor $\exp(\pi\mu)$ proves to be so large that the oscillations are not manifested. Taking account of rotation in the final state has been studied in Ref. 120 (some discussion of this analysis has been presented in Sec. 3d), where it was shown that, in principle in this case, a resonance can appear near the threshold, but its width is so small that it may not be manifested experimentally. Similar resonances have been obtained in certain calculations within the framework of the strong-coupling method,[212,213] and have been identified, erroneously as we see it, as corresponding to the experimental data.[185]

Second, the dipole interaction can substantially alter the threshold behavior of the width of the resonance, as has been pointed out in Refs. 182, 183, and 210, and thus affect the threshold behavior of the cross-sections to a considerably greater extent than the interaction in the final state discussed above.

Apparently a virtual intermediate state is not a rarity, especially for heteronuclear molecules for which no restrictions on parity are imposed on the orbitals. However, the influence of a virtual state on the process of vibrational excitation will not always be appreciable. The point is, as we

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have already pointed out, that, along with the virtual prolongation of the bound state, a virtual pole of the adiabatic S-matrix must exist in the system, which meets with this state on the negative imaginary semiaxis. If the point of this meeting is close to zero, then the virtual character of the state is manifested in the cross-sections only in the immediate vicinity of the threshold. At higher energies, when the behavior of the term of the intermediate state becomes essential far from its point of emergence into the continuous spectrum, this state can be treated as quasistationary. Nevertheless, cases apparently exist in which the virtual character of the intermediate state is manifested over a broad energy range. This statement is confirmed by experiments[188] in which rather sharp maxima were observed near the thresholds for a number of molecules. In the case of a quasistationary intermediate state, such sharp maxima could arise only with a small width, while then, as we see it, they must give rise to an oscillatory structure in the cross-sections similar to that observed for the N_2, CO, and CO_2 molecules.

In closing we should point out some studies of collisions of slow electrons (energy < 1 eV) with CO_2 molecules. It has been noted[88,214,215] that a virtual state arises in such collisions. The method applied in Refs. 214 and 215 can be considered intermediate between *ab initio* calculations and the modeling approach. Despite the complexity of the system being treated and the semiphenomenological assumptions adopted concerning the interaction of the electron with the molecule, the cited studies have reproduced a series of experimental results. In particular, they have shown that a virtual state leads to a sharp increase in the elastic cross-section[88] and the cross-section for the transition $(0,0,0) \rightarrow (1,0,0)$[214,215] near the threshold.

CONCLUSION

On the basis of the material presented above, we can note that, although the physics of electron-molecule collisions is far richer and more complex than the physics of electron-atom collisions, substantial progress has been made recently in qualitative understanding and quantitative description of the processes of electron-molecule scattering. However, a large number of problems remains, involved both with perfection of the experimental technique and the theoretical methods of calculation with the aim of obtaining more accurate quantitative characteristics, and with the qualitative understanding of the physics of certain processes.

We believe that the following are the key problems at present. In the experimental measurements one must develop a methodology of obtaining and working with monokinetic beams of slow electrons and substantially increase the accuracy of measuring the final channels. In the theoretical studies, the most vital problem is that of elucidating the role of the long-range dipole interaction in the formation of near-threshold maxima in the cross-sections for vibrational excitation of the hydrogen halides. Along with these problems, one must obtain the most reliable information, both experimental and theoretical, on the processes of collision of electrons with molecules of practical interest.

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