- ⁶V. A. Bazylev and N. K. Zhevago, Zh. Eksp. Teor. Fiz. 69, 853 (1975) [Sov. Phys. JETP 42, 436 (1976)].
- ⁷V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 66, 1981 (1974) [Sov. Phys. JETP **39**, 975 (1974)].
- ⁸R. Z. Vitlina, A. V. Chaplik, and M. V. Éntin, Zh. Eksp. Teor. Fiz. 67, 1667 (1974) [Sov. Phys. JETP 40, 829 (1975)].
- ⁹E. E. Nikitin, Teoriya élementarnykh atomno-molekulyarnykh reaktsii (Theory of Elementary Atomic-Molecular Reactions), Novosibirsk (1971).
- ¹⁰L. D. Landau, Phys. Z. Sowjetunion 2, 41 (1932).
- ¹¹C. Zener, Proc. R. Soc. Lond. A137, 696 (1932).
- ¹²Yu. N. Demkov, Zh. Eksp. Teor. Fiz. 45, 195 (1963) [Sov. Phys. JETP 18, 138 (1964)].
- ¹³B. M. Smirnov, Asimptoticheskie metody v teorii atomnykh

stolknovenii (Asymptotic Methods in the Theory of Atomic Collisions), Atomizdat, 1973.

- ¹⁴N. Rozen and C. Zener, Phys. Rev. 40, 502 (1932).
- ¹⁵N. Mott and G. Massey, Theory of Atomic Collisions (Russ. Transl., "Mir," M., 1969).
- ¹⁶R. H Dicke, Phys. Rev. **93**, 99 (1954).
- ¹⁷R. Kh. Propin, Opt. Spektrosk. 8, 300 (1960); 10, 308 (1961).
- ¹⁸V. Fano, Phys. Rev. **124**, 1866 (1961).
- ¹⁹Y. Pietenpol, Phys. Rev. 162, 1301 (1967).
- ²⁰K. Katzuura, J. Chem. Phys. 42, 3771 (1965).
- ²¹B. M. Smirnov and O. B. Firsov, Pis'ma Zh. Eksp. Teor. Fiz. 2, 478 (1965) [JETP Lett. 2, 297 (1965)].

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Decay and excitation of a quantum system following two successive sudden changes in the Hamiltonian

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The response of a quantum system to two successive sudden changes of the Hamiltonian is considered. The dependence of the probabilities for various processes on the dwell time τ of the system in the intermediate state is investigated, the interaction in the intermediate state being represented by a repulsive potential of the form γ/r^2 . Analytic expressions are found for the limiting cases of large and small values of τ . The deviations of the spectra of the dissociation products of diatomic molecules from the Franck-Condon distribution for resonance scattering of electrons is investigated in detail. A possible isotope effect for hydrogen molecules is noted.

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1. The problem of the transitions of a quantum system described by a time dependent Hamiltonian arises in the treatment of various processes involving the interactions of atoms and molecules. Such problems do not admit of exact solution if the transitions in the continuous spectrum are to be taken into account, and most of the known results either relate to special model Hamiltonians or have been obtained within the limitations of time dependent perturbation theory. Here we examine the reaction of a quantum system to two successive sudden changes of the Hamiltonian $H(r, t)^{1}$:

$$H(r,t) = \begin{cases} H_{\alpha}(r), & t < 0\\ H_{int}(r), & 0 < t < \tau. \\ H_{s}(r), & \tau < t \end{cases}$$
(1)

Here H_{α} and H_{β} are the initial and final Hamiltonian, and τ is the dwell time of the system in the intermediate state described by Hamiltonian H_{int} . Such a problem was first formulated for a zero-range potential model under the initiative of Yu. N. Demkov, and the ejection of a weakly bound electron in an atomic collision was treated by Bronfin and Ermolaev^[2] as an example.

However, it is easy to exhibit a wide range of physical processes and systems involving successive fast changes in the character of the binding in which the interactions are of a more complicated type. As an example we might consider processes in which the outer electron shells of atoms are reconstituted as a result of a cascade of nuclear transformations (in which the nuclear charge or the effective charge of the core of tightly bound electrons suffers changes). Specifically, we might speak of a sequence of β^+ and β^- decays of a heavy nucleus, of the nuclear photoeffect $_{Z}A^{N}(\gamma,_{1}H^{1})_{Z-1}A^{N-1}$ (with subsequent ejection of a K electron by a γ ray from the excited product nucleus $_{Z-1}A^{N-1}$), etc.

The resonance scattering of an electron by a diatomic molecule,

$$e^{-} + AB(v) \rightarrow (AB)^{-}$$
, (2)
 $e^{-} + A + B$

may serve as another example. As can be shown, the theoretical treatment of this process involves a stage in which the problem of the reaction of the nuclear subsystem to two successive sudden changes in the interatomic potential must be solved. In fact (see, e.g., $[^{3-6}]$), the amplitude for process (2) has the form (except for a constant factor)

$$A_{ij} = \sum \frac{\langle \varphi_j | \overline{\gamma \Gamma} | \chi_{\mu} \rangle \langle \chi_{\mu} | \overline{\gamma \Gamma} | \varphi_i \rangle}{\varepsilon - \varepsilon_{\mu} + i \Gamma_{\mu}/2} = \int d\mathbf{r} \, \varphi_j(\mathbf{r}) \, \overline{\gamma \Gamma(r)} \, \zeta(\mathbf{r}).$$
(3)

Here $\varphi_{i(f)}$ and χ_{μ} are the wave functions for the initial (final) and intermediate states of the nuclear subsystem

(the subscripts *i* and *f* label the initial and final states, and the summation is taken over all intermediate states), $\Gamma(r)$ is the autoionization width of the ionic term, Γ_{μ} is the total width of the μ -th level of the AB⁻ complex, whose energy ε_{μ} is reckoned from the initial energy of the nuclear subsystem, ε is the energy of the incident electron, r is the difference between the position vectors of the two nuclei, and $\zeta(r)$ is a solution of the equation^[3,4]

$$(E+i/_{2}\Delta-V(r))\zeta(r) = -\varphi_{i}(r)\sqrt[\gamma]{\Gamma(r)}, \qquad (4)$$

in which V(r) is the complex potential for the interaction of the atoms in the quasimolecule AB⁻, i. e., $V = U(r) - (\frac{1}{2})i\Gamma(r)$ ($\hbar = m_e = e = 1$).

Introducing the Green's function for Eq. (4), we can write Eq. (3) in the form

$$A_{ij} = \int d\mathbf{r} \, d\mathbf{r}' \, \varphi_j \Gamma^{\nu_b} G(\mathbf{r}, \mathbf{r}') \, \Gamma^{\nu_b} \varphi_i. \tag{5}$$

If we neglect the variation of $\Gamma(r)$ in the fundamental transition region (in this connection see^[3,5,6]) and perform a Fourier transformation, we can write Eq. (5) in the following form, which involves only a single integration:

$$A_{ij} = -i\Gamma \int d\tau \, a_{ij}(\tau) \exp(i\varepsilon \tau - \frac{i}{2}\Gamma \tau), \qquad (6)$$

• where

$$a_{ij}(\tau) = \sum_{\mu} \langle \varphi_j | \chi_{\mu} \rangle \langle \chi_{\mu} | \varphi_i \rangle \exp(-i\varepsilon_{\mu}\tau)$$
(7)

is the probability amplitude for an intramolecular transition following two successive sudden changes in the interatomic potential at times t=0 and $t=\tau$.

It should be noted that the features of the quantum transitions considered below as functions of the dwell time of the system in the intermediate state are also of interest in connection with other physical processes and systems. For example, the collision of a fast atom with a molecule may involve two passages through the region of strong nonadiabatic coupling. Then at points of pseudocrossing of terms, an electronic transition is instantaneous as compared with the vibrational motion of the molecule provided $a \ll v/\omega$, where a is the size of the nonadiabatic transition region, v is the velocity of the incident atom, and ω is the vibrational frequency of the molecule.

Related problems also arise in the treatment of the interaction of heavy dipole molecules with ultrashort laser-light pulses, the reaction of an atomic system to the sudden application of a magnetic field, ^[7] etc.

The time dependent Green's function

$$G_{int}(t) = \sum_{\mu} |\chi_{\mu}\rangle \langle \chi_{\mu}| \exp\left(-i\epsilon_{\mu}t\right) = \left(i\frac{\partial}{\partial t} - H_{int}\right)^{-1}, \qquad (8)$$

which describes the evolution of the system during the time τ , is known in explicit form only for a limited number of Hamiltonians. The case of the oscillator poten-

tial, corresponding to a transition between vibrational states of the intermediate complex AB⁻, has been well investigated in published studies.^[3,4,6] Below, we use the model Hamiltonian

$$H_{\rm int} = -\frac{1}{2}\Delta + \gamma/r^2 \tag{9}$$

to discuss features of intramolecular transitions via the formation of an AB⁻ ion with a repulsive potential. The interaction potential γ/r^2 admits of analytic treatment²) and (with $\gamma > 0$) gives a reasonable approximation to the actual terms of negative ions, which are characterized by a force that decreases with increasing internuclear distance r and an interaction that vanishes in the limit $r \rightarrow \infty$. This same approximation has been used by Chen and Magee^[5] in treating the resonance vibrational excitation of hydrogen molecules (in each special case the value of γ can be chosen in accordance with the force acting in the fundamental transition region).

Using the expansion of the known expression for the operator $(i\partial/\partial t + \Delta/2)^{-1}$ in spherical harmonics, it is not difficult to show that

$$\left(i\frac{\partial}{\partial t}+\frac{1}{2}\Delta-\frac{\gamma}{r^2}\right)^{-1}=\frac{i^{3\lambda+1}}{4\pi rr'\sqrt{t}}u_{\lambda}\left(\frac{rr'}{t}\right)\exp\left\{i\frac{r^2+r'^2}{2t}\right\},$$

where the function $u_{\lambda}(z) = z^{1/2}J_{\lambda}(z)$ satisfies the equation

$$(1+\Delta-2\gamma/z^2)u_{\lambda}(z)=0, \ \lambda=(2\gamma+1/4)^{1/2}.$$

Thus, the problem reduces to the calculation of integrals of the form

$$a_{\alpha\beta}(\tau) = \frac{i^{3\lambda+1}}{\sqrt{\tau}} \int dr \, dr' \, R_{\alpha}(r) R_{\beta}(r') \, u_{\lambda}\left(\frac{rr'}{\tau}\right) \exp\left\{i\frac{r^2+r'^2}{2\tau}\right\}, \qquad (10)$$

in which R_{α} and R_{β} are the radial wave functions for the initial (α) and final (β) states of the system. The values of the transition integrals (10) are determined by the relationships obtaining among the characteristic time parameters τ , $a_{\alpha(\beta)}$, $\omega_{\alpha(\beta)}^{-1}$, and k^{-2} of the system, where $a_{\alpha(\beta)}$ is the characteristic region of motion in the bound initial (final) state, $\omega_{\alpha(\beta)}$ is the characteristic frequency of transitions to the discrete spectrum of Hamiltonian $H_{\alpha}(H_{\beta})$, and k is the relative momentum of the particles (for transitions to the continuous spectrum). Let us consider the two limiting cases in which the time τ during which the perturbation acts is respectively short and long.

2. When the time τ during which the perturbation acts is short and $H_{\alpha} = H_{\beta}$ (this is the case of greatest interest for the study of fast atomic-nuclear processes) the initial state will obviously be only slightly altered. As can be seen, however, this condition is not enough for the applicability of time dependent perturbation theory. So let us write Eq. (7) in integral form:

$$a_{ij}(\tau) = \int \frac{d\mathbf{k}}{(2\pi)^3} f_{ik} f_{jk} \exp\left(-i\frac{k^2\tau}{2}\right)$$
(11)

(we are thinking of a transition between states i and j of the Hamiltonian H_{α}), where the

$$f_{i(j)k} = \langle \varphi_{i(j)} | \chi_{k} \rangle = \frac{\pi \sqrt{2}}{k} \int dr \, R_{i(j)}(r) \, u_{\lambda}(kr) \tag{12}$$

are the overlap integrals of the wave functions for the initial (final) state of the quantum system with the wave functions of the intermediate Hamiltonian H_{int} . The time dependent perturbation series corresponds to an expansion of amplitudes (7) in integral powers of τ , an expansion that can be formally obtained by expanding the exponential $\exp(-ik^2\tau/2)$ under the integral sign in (11). If the corresponding product of overlap integrals (12) decreases with increasing k faster than any power (e.g., exponentially, as is the case for Hamiltonians of the harmonic oscillator type, whose states belong to a discrete spectrum), the perturbation series will converge uniformly. In the most interesting cases, however (when, for example, the Hamiltonians $H_{\alpha(\beta)}$ have a continuum of states in addition to the discrete spectrum), integrals (12) fall off at infinity according to a power law: $f_{i(j)k} \propto k^{-n_i(j)}$, and the terms of the formal perturbation series diverge, beginning with n + 1 $(n = E(\nu - 1)/2)$ 2), where $\nu = n_i + n_j - 3$). In this case we have the asymptotic expansion

$$a_{ij}(\tau) = \sum_{m=0}^{\infty} b_{ij}^{(m)} \tau^m + (-i\tau)^{\nu/2} \sum_{p,q=0}^{\infty} \sum_{c_{ij}}^{(p,q)} \tau^{(p+q)/2}, \qquad (13)$$

which can be derived by breaking up the integration in (11) into two regions, expanding $\exp(-ik^2\tau/2)$ in the first region, and using the asymptotic series

$$f_{ik}f_{jk} = \sum_{p,q=0}^{\infty} \frac{A_{ip}A_{jq}}{p!q!} (\epsilon_i^p \epsilon_j^q)^{\frac{N}{2}} k^{-(n_i+n_j+p+q)},$$

$$k \gg \max(\epsilon_i, \epsilon_j)^{\frac{N}{2}}$$

for the products of overlap integrals in the second region (here ε_i and ε_j are the energies of the initial and final states). Then the terms of expansion (13) are determined as the corresponding inverse images (from the expansions about zero and at infinity). The coefficients in formula (13) can be easily calculated; in particular, for the $c_{ij}^{(p,q)}$ we have

$$c_{ij}^{(p,q)} = -\frac{A_{ip}A_{jq} \cdot \left[(-i\varepsilon_i)^p (-i\varepsilon_j)^q\right]}{2\pi^2 p! q! (\nu + p + q)!!} {i\sqrt{\pi/2} \choose \frac{1}{2}C\gamma_i}$$

in which the upper (lower) quantity in the large parentheses is for odd (even) values of $\nu + p + q$ ($\nu + p + q = 2s$ + 1 or $\nu + p + q = 2s$, where s = 0, 1, 2, ...) and C is Euler's constant.

According to formula (13) only the first *n* terms can be found by time dependent perturbation theory: the subsequent terms of the expansion, which take all the virtual transitions to the continuous spectrum accurately into account, cannot be calculated by time dependent perturbation theory.³⁾ Asymptotic expansions of the type of (13) obtain for analytic Hamiltonians $H_{\alpha,\beta}$. For nonanalytic potentials $V_{\alpha,\beta}$ (of the square well type) the $a_{i,j}(\tau)$ have essential singularities at zero, but even in this case the first few terms of the expansion can be found by time dependent perturbation theory (the zerorange potential is an exception: for it, perturbation theory cannot be applied at all).

3. When the perturbation time τ is long (this is the case of greatest interest for processes of the type of

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(2)) the system decays with a probability close to unity. In this case the leading approximation gives the Franck-Condon distribution for the decay products:

$$a_{\alpha\beta}(\tau \to \infty) = \overline{\sqrt{\pi/2}} \int dr \, R_{\alpha}(r) \, u_{\lambda}(kr),$$

which corresponds to a transition to the continuous spectrum under the action of a single sudden change H_{α} – H_{int} of the Hamiltonian. Let us take the finite values of τ into account in investigating the excitation probability and the deviation from the Franck-Condon distribution.

For the case of transitions between discrete levels, when $\tau \gg \tau_{\max} = \max(a^2, \omega^{-1})$, the main contribution to the excitation integrals comes from the values of r and r'that correspond to a small value for the argument of the function $u_{\lambda}(rr'/\tau)$. Then in the leading approximation in powers of $1/\tau$ we have the following expression for the amplitude for the $\alpha - \beta$ transition⁴:

$$a_{\alpha\beta}(\tau) = \frac{i^{3\lambda+i} \bar{I}_{\alpha} \bar{I}_{\beta}}{2^{\lambda} \Gamma(\lambda+1) \tau^{\lambda+i}},$$
(14)

$$\bar{I}_{\alpha(\beta)} = I_{\alpha(\beta)}(\infty), \quad I_{\alpha(\beta)}(\tau) = \int r^{\lambda + l_{\beta}} R_{\alpha(\beta)}(r)^{ir^{3/2\tau}} dr,$$
(15)

i.e., the dependence of the excitation probability on the duration τ of the perturbation is mainly determined by the force *F* acting on the system in the intermediate state $(F_{\max} \propto (\lambda^2 - \frac{1}{4})/\rho_0^3)$, where ρ_0 is the size of a typical region of localization of the initial bound state).

In considering transitions to the continuous spectrum we express the final-state wave function as the sum of an incident wave $R_E^{(-)}(r')$ and a reflected wave $R_E^{(+)}(r')$ $(E = k^2/2)$ and shift the integration contour in the complex r' plane away from the real axis, integrating the term containing $R_E^{(+)}(r')$ along the ray $\arg r' = \pi/4$ and the term containing $R_E^{(-)}(r')$ along the contour shown in Fig. 1. When $\tau \gg \tau_{\max} = \max(a^2, \omega^{-1}, k^{-2})$ the integrals along the ray arg $r' = \pi/4$ converge rapidly in the neighborhood of the origin and make a contribution of ~ $1/\tau^{\lambda+1}$ to the probability amplitude for a transition to the continuous spectrum. All possible singularities of $R_E(r')$ in the complex plane (poles and branch points) lie at finite distances (independent of τ) and also introduce contributions of ~ $1/\tau^{\lambda+1}$ ($\lambda > 1$). The remaining integral, taken along the line $\arg(r' - k\tau) = \pi/4$, is determined by the neighborhood of the point $k\tau$, which is fairly far from the origin. Hence for $k^2 \tau \gg 1$ and potentials $V_{\beta}(r')$ that fall off rapidly at infinity $(V_{\beta} \sim (r')^{-n}$ with n $\geq \lambda + 1$), we obtain

$$a_{\alpha E}(\tau) = \exp\left\{-i\delta_{\lambda}(E) + \frac{i}{2\tau}\Delta_{\lambda}\right\} \bar{a}_{\alpha E}(\tau) + O\left(\frac{1}{\tau^{\lambda+1}}\right), \qquad (16)$$

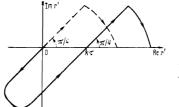


FIG. 1. Integration contours. The dashed (full) contour is for the integral containing $R_E^{(+)}(r')$ $(R_E^{(-)}(r'))$.

where

$$\bar{a}_{\alpha E}(\tau) = \sqrt{\frac{\pi}{2}} \int dr \, R_{\alpha}(r) \, u_{\lambda}(kr) \, e^{irt/2\tau}, \quad (\operatorname{Im} \delta_{\lambda}(E) = 0).$$
$$\delta_{\lambda}(E) = E\tau + \delta(k) + \frac{1}{2}\pi \, (\lambda - \frac{1}{2}).$$

Formula (16) gives the Franck–Condon distribution in the leading approximation; the corrections to this distribution are associated with the finite time for reduction in the intermediate potential of the wave packet describing the initial state. If the repulsion in the intermediate state is strong enough ($\lambda > 1$) the spectrum of the decay products is determined to terms of the order of $1/\tau^{\lambda+1}$ by the first term in (16). To the same approximation, the total decay probability

$$\int_{0}^{\infty} dk \exp\{i\Delta_{k}/2\tau\} \bar{a}_{aE}(\tau)$$

$$\times \exp\{-i\Delta_{k}/2\tau\} \bar{a}_{aE}(\tau)$$
(17)

is unity. This can be easily seen directly by expanding one of the exponentials in (17) (which contains the differential operator Δ_k) and integrating the resulting series by parts.

If the leading correction term is taken into account, the energy spectrum of the decay products, according to (16), will have the form

$$w_{aE}(\tau) = (1 + \Lambda(\tau)) \overline{w}_{aE}, \qquad (18)$$

where

$$\Lambda(\tau) = \frac{3\gamma}{4(E\tau)^2} \left(\frac{2}{3} E \frac{\partial}{\partial E} - 1 \right)$$

is an operator describing the distortion of the spectrum $\overline{w}_{\alpha E} = |\overline{a}_{\alpha E}(\infty)|^2$ obtained in the Franck-Condon approximation as a result of the finite time of action of the perturbation. In particular, for an initial state localized in a neighborhood of $\rho_0 (R_{\alpha} \sim \exp(-(r-\rho_0)^2/a^2))$ with $a \ll \rho_0$, Eq. (18) takes the form

$$w_{aE}(\tau) = w_0(1 + \Lambda(\tau)) \left| \exp\left(\frac{a^2}{4} \frac{\partial^2}{\partial \rho_0^2}\right) u_\lambda(\rho_0 \sqrt{2E}) \right|^2.$$
(19)

It follows from Eqs. (18) and (19) that taking into account the finite time τ during which the perturbation acts, broadens the spectrum (in connection with the additional quantum indeterminancy) and shifts the peak of the distribution toward the lower energies (owing to the finite time during which the force F acts in the intermediate state). The physical consequences of this conclusion are discussed in Sec. 5.

Spectrum (18) may be characterized by two parameters: the energy at the peak of the Franck-Condon distribution $(E_0 = \gamma/\rho_0^2)$ and the force F acting on the particle in the fundamental region $|r - \rho_0| \sim a$ of motion in the initial state; and in this form the spectrum reflects the features of any monotonically decreasing repulsive potential V_{int} .

4. Equations (14) and (16), obtained above, are valid for asymptotically large values of τ ($\tau \gg \tau_{max}$). For smaller values of τ the probability for finding the particle at a finite distance r and various transition probabilities are determined by the interference of two waves, one of which describes the outward motion of the particle to infinity after having been reflected from the potential barrier at distances $r \sim (\gamma/E)^{1/2}$. For example, in the case of a localized initial state, the probability for the elastic process when $\rho_0 a < \tau$ (when the wave packet extends beyond the limits of the initial localization) is given by

$$w_{\alpha\alpha}(\tau) \sim (a\rho_0/\tau)^2 J_{\lambda}^2(\rho_0^2/\tau).$$

In the opposite case of a quasiclassical initial state, when $p_n d \sim \varkappa_n d \gg 1$ and $\gamma = 0$ (*d* is the characteristic size of the potential well and p_n and \varkappa_n are the momenta of the bound state inside and outside the well), for small times τ satisfying $p_n^{-2} \ll \tau \ll p_n^{-1} d$ the interference is not important and the probability for the elastic process is

 $w_{nn}(\tau) \approx 1 - p_n \tau/d$

in accordance with the classical picture of the motion of the initial state wave packet. For large τ ($\tau \gg p_n^{-1}d$) we have

$$w_{nn}(\tau) \approx \frac{2}{\pi (p_n d)^2 (p_n^2 \tau)} \sin^2 \frac{d^2}{\tau}.$$

5. Let us use the results obtained in Sec. 3 to discuss the features of the spectrum of the dissociation products of hydrogen molecules incident to resonance interaction with electrons (process (2)). Using formulas (6), (16), and (18) with $|E - E_0| < E_0$ and $\Gamma \ll E_0$ and explicitly exhibiting the dependence of the model parameters on the reduced mass μ of the molecule, we can put the spectrum of the dissociation products in the form

$$W_{\alpha E}(E) \approx \left\{ 1 + \frac{3\gamma \mu \Gamma^2}{16E^2} \left[\frac{16E(E_0 - E)}{3\Omega^2} - 1 \right] \right\} \overline{w}_{\alpha E},$$
(20)

where

$$\Omega = \frac{2\sqrt{2}}{\sqrt{\mu\omega}} \left| \frac{dV_{int}}{dr} \right|_{\rho}$$

is the width of the peak of the Franck-Condon spectrum and ω is the vibrational frequency. The Franck-Condon distribution for the decay products is compared in Fig. 2 with the distribution calculated with Eq. (20) for an electron energy ε corresponding to excitation of the H₂⁻ autoionization state $(1s\sigma_{\epsilon})(2p\sigma_{u})^{2}\Sigma_{\epsilon}^{*}$. It is not difficult to see that in this case the shift of the peak of the Franck-Condon spectrum due to the finite dwell time of the system in the intermediate autoionization state of H₂⁻ is given in the leading approximation in the parameter $\delta = \Gamma/E_0$ by

$$\Delta E = E_0 - \overline{E} \approx \frac{1}{8} \mu \gamma E_0 \delta^2.$$

From this it follows that the spectrum of the decay products will be broader and its peak will be shifted to lower energies for heavier isotopic variants of the molecule. In particular, the shifts ΔE of the peaks for H₂, HD, and D₂ molecules satisfy the condition

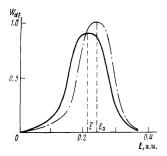


FIG. 2. Comparison of the Franck-Condon distribution for the products of the resonance dissociation of hydrogen molecules (process (2)) with the distribution calculated with Eq. (20) using the parameter values $E_0 \approx 2.4 \cdot 10^{-1}$ and $\Omega \approx 1.5 \cdot 10^{-1}$ from^[6] and the experimental value $\Gamma \approx 7.4 \cdot 10^{-3}$ from^[9]. The dashdot curve shows the Franck-Condon spectrum normalized to unity at the peak, and the full curve shows the spectrum calculated with allowance for the finite dwell time of the system in the $(1 s\sigma_{e})(2p\sigma_{w})^{2}\Sigma_{e}^{*}$ state of H₂⁻.

 $\frac{\Delta E(D_2) - \Delta E(H_2)}{\Delta E(HD) - \Delta E(H_2)} = 3$

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¹⁾Transitions following a single rapid change of the interaction are described by the theory of sudden perturbations and have been well investigated for specific systems.^[1]

- ²⁾Earlier published papers on the resonance interaction of electrons with molecules were based on numerical integration of Eq. (4) or on direct summation of expression (3).
- ³⁾As a specific example we give the asymptotic expansion of the amplitude for the elastic process following sudden removal of the Coulomb potential with its subsequent restoration a time τ later $(V_{\alpha} = V_{\beta} = -z/r, R_{\alpha} = R_{\beta} = 2rz^{3/2}e^{-rr})$:

$$a_{ii}(\tau) = 1 - i \frac{z^2 \tau}{2} - \frac{5}{8} (z^2 \tau)^2 + \frac{32}{15} \left(\frac{i}{2\pi}\right)^{\frac{1}{2}} (z^2 \tau)^{\frac{5}{2}} + \cdots$$

- ⁴⁾The known result $a_{\alpha\beta} \sim \tau^{-3/2}$ for free motion in the intermediate state (see, e.g., ^[8]) follows from Eq. (14) with $\lambda = 1/2$ ($\gamma = 0$).
- ¹L. D. Landau and E. M. Lifshits, Kvantovaya mekhanika (Quantum mechanics), Fizmatgiz, 1963.
- ²F. B. Bronfin and A. I. Ermolaev, Vestnik LGU 22, 29 (1971).
- ³J. N. Bardsley, A. Herzenberg, and F. Mandl, Proc. Phys. Soc. Lond. 89, 305 (1966).
- ⁴D. T. Birtwhistle and A. Herzenberg, J Phys. B 4, 53 (1971).
- ⁵J. C. Y. Chen and J. L. Magee, J. Chem. Phys. 36, 1407 (1972).
- ⁶J. C. Y. Chen, J. Chem. Phys. 40, 3513 (1964).
- ⁷G. V. Skrotskii and G. I. Solomakho, Opt. Spektrosk. 39,
- 827 (1975) [Opt. Spectrosc. (USSR) 39, 470 (1975)].
- ⁸Yu. N. Demkov, Zh. Eksp. Teor. Fiz. 46, 1126 (1964) [Sov. Phys. JETP 19, 762 (1964)].

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Stimulated Raman emission and frequency scanning in an optical waveguide

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Equations are derived for stimulated Raman emission in an optical waveguide. The arbitrary number of components of the radiation and also the dependence of the refractive index on the light intensity are taken into account in the equations. Solutions of the equations are obtained for some cases of practical interest. On the basis of the solutions the following phenomena are predicted and investigated: "ladder" scanning of the optical frequency in a fixed cross section of the waveguide; a "multiplication" effect of the initial scanning range due to mutual transformation of the radiation components; the possibility of controlling the scanning process by means of a weak input (Stokes) pulse. The possibilities of "quenching" stimulated Raman emission in a wave guide are also considered.

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INTRODUCTION

It is known that various nonlinear phenomena can be observed in optical waveguides. Ippen *et al.*^[1] have observed broadening of the spectrum of picosecond light pulses passing through a multimode optical waveguide. This broadening was attributed by them to phase modulation due to the dependence of the refractive index of the waveguide material on the light intensity. In an earlier paper⁽²⁾ I called attention to the fact that the passage of an intense light pulse with an initially fixed field-oscillation frequency through a single-mode optical waveguide can be used to obtain¹⁾ broadband scanning of the frequency in this pulse, such that the scanning interval can exceed, for example, 10^{14} rad/sec.

Frequency scanning uncovers great possibilities for selective excitation of a specified level of multilevel

⁹G. V. Dubrovsky, V. D. Ob'edkov, and R. K. Janev, V. ICPEAC, Abstracts of papers, Leningrad, 1967.