Antibonding intermediate state in the theory of vibrational excitation of diatomic molecules by slow electrons

A. K. Kazanskiĭ

Leningrad State University

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An exactly solvable model is constructed for the description of the processes that take place when a slow electron collides with a diatomic molecule (vibrational excitation, associative detachment, and dissociative attachment). As a particular model of the variant, the case of an antibonding (virtual) state of an intermediate state is considered, and a term of this state is parametrized in a very simple manner. The vibrational excitation and dissociative attachment are calculated for a system corresponding to the HCl molecule. The results are in good qualitative agreement with experiment.

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1. Vibrational excitation of diatomic molecules plays an essential role in the kinetics of a low-temperature gas-discharge plasma. Experimental investigation of this process is frequently very complicated.[1] In particular, great difficulties are encountered in the study of hydrogen halide molecules because of their chemical activity. Particular interest in this molecules was aroused by experiments[2] in which sharp threshold peaks were observed in the vibrational-excitation cross sections. These singularities were attributed in the first studies to the long-range interaction of the molecule and the electron, an interaction determined by the electric properties of the molecule. However, observation of similar singularities also in the cross sections for vibrational excitation of the symmetric molecules SF_6 and CH_4 (Ref. 3) has led to a new explanation based on the concept of the virtual intermediate state[4] analogous to the known compound state of the N_2 molecule. The term of the molecular ion HCl^- was calculated by the stabilization method.[5] The result of that study can be treated[6] as indirect evidence of the virtual character of the HCl^- complex. The process $e+HF$ was also calculated and the results agreed qualitatively with experiment.[7] The last cited references considered electron scattering by the charge distribution in the HF molecule, and the intermediate HF^- state was not investigated.

The problem of theoretically investigating the singularities of vibrational excitations via a virtual intermediate state was discussed in Refs. 11–14. The most advanced is the investigation of an exactly solvable model[12-14] in which a parabolic approximation is assumed for the potential well of the molecule, as well as a separable approximation for the description of the states of the discrete and continuous spectra.

We propose in this paper a model that permits an exanalysis of the role of the intermediate antibonding (virtual) state in vibrational excitation processes. This model is similar to the one proposed earlier[8-9] and is specified by the Hamiltonian (in atomic units)

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

Here R is the distance between nuclei, M is the reduced mass of the nuclei, and l and ω are parameters that characterize the interaction of the nuclei in a neutral molecule. The electron is described by the variable r and interacts with the molecule through a long-range potential $V(r)$ that is independent of the variable R, and a separable potential that depends on this variable;

$$\hat{H}_0=-{}^1/{}_2\partial^2/\partial r^2+V(r).$$

The functions $\varphi(r)$ and $V(r)$ will be assumed real and spherically symmetrical.

In the immobile-nuclei approximation, the system (1) has a continuous spectrum (with respect to the electron coordinate) with end point

$$U_0(R)=l(l+1)/2MR^2+M\omega^2R^2/2 \quad (2)$$

and a bound state (as $R\to\infty$). The bound-state term is determined by the set of equations

$$\begin{gathered}T(R)=U_0(R)+\varepsilon(R),\\ \langle\varphi|(\hat{H}_0-\varepsilon(R)+i0)^{-1}|\varphi\rangle=-\beta^{-1}(R^2-R_0^2)^{-1}.\end{gathered} \quad (3)$$

At a certain R_1 the function $\varepsilon(R_1)=0$ and the term $T(R)$ crosses the boundary of the continuous spectrum $U_0(R)$. It will be shown below that all the physical characteristics of the system are determined by the term T and do not depend explicitly on the "bare" constants β, R_0, $\varphi(r)$, and $V(r)$.

The proposed model satisfies the following three requirements:

1) the quantum character of the nuclear motion is explicitly taken into account;

2) the character of the term that goes off to the continuous spectrum remains sufficiently arbitrary;

3) all the channels of the process can be calculated simultaneously and without any additional approximations, including the dissociative-attachment and associative-detachment reactions.

Only one exactly solvable model satisfying the first requirement was proposed previously,[10] but the term in that model was taken to be practically single-valued and was not realistic enough.

2. We seek the solution of the eigenfunction problem

$$\hat{H}|\Psi(R)\rangle=E|\Psi(R)\rangle,\quad |\Psi(0)\rangle=0, \quad (4)$$

in the form of the series

$$|\Psi(R)\rangle=\sum_{n=0}^{\infty}\chi_n(R)|c_n\rangle, \tag{5}$$

where

$$\chi_n(R)=(M\omega)^{1/4}[2n!/\Gamma(n+l+{}^3/_2)]^{1/2}\tilde{R}^{l+1}\exp(-\tilde{R}^2/2)L_n{}^{l+1/2}(\tilde{R}^2),$$
$$\tilde{R}=R(M\omega)^{1/2}.$$

To determine the vectors $|c_n\rangle$ we have the following system of equations:

$$\begin{gathered}E|c_k\rangle=E_k|c_k\rangle+\hat{H}_0|c_k\rangle-\beta R_0{}^2|\varphi\rangle\langle\varphi|c_k\rangle\\+(\beta/M\omega)|\varphi\rangle\hat{Q}\langle\varphi|c_k\rangle,\quad |c_{-1}\rangle=0;\\(\hat{Q}a)_k\equiv(2k+l+{}^3/_2)a_k-[k(k+l+{}^1/_2)]^{1/2}a_{k-1}\\-[(l+k+{}^3/_2)(k+1)]^{1/2}a_{k+1},\quad E_k=\omega(2k+l+{}^3/_2).\end{gathered} \tag{6}$$

We consider first the process of inelastic scattering of an electron having an energy ε and a wave vector **q** by a molecule in an initial vibrational state n_0, $E=\varepsilon+E_{n_0}$. This process is described by a solution of (6) in the form

$$|c_n\rangle=|\zeta_{\mathbf{q}}\rangle\delta_{nn_0}+a_n\hat{G}^+(\varepsilon_n)|\varphi\rangle\langle\varphi|\hat{G}^+(\varepsilon_n)|\varphi\rangle^{-1}, \tag{7}$$

where

$$\varepsilon_n=E-E_n,\quad (\hat{H}_0-\varepsilon)|\zeta_{\mathbf{q}}\rangle=0,$$
$$|\zeta_{\mathbf{q}}\rangle\sim e^{i\mathbf{qr}}+f(\theta)e^{iqr}/r,\quad \theta=(\widehat{\mathbf{q},\mathbf{r}}),$$
$$\hat{G}^\pm(\varepsilon)=(\hat{H}_0-\varepsilon\pm i0)^{-1},$$

$f(\theta)$ is the amplitude of the potential scattering for the Hamiltonian H_0. Substitution of (7) in (6) leads to the recurrence relations (*RR*)

$$-R^2(\varepsilon_n)a_n+\frac{1}{M\omega}\hat{Q}[\langle\varphi|\zeta_{\mathbf{q}}\rangle\delta_{nn_0}+a_n]=R_0{}^2\langle\varphi|\zeta_{\mathbf{q}}\rangle\delta_{nn_0}. \tag{8}$$

It is convenient to introduce the sequence

$$b_n=(\langle\varphi|\zeta_{\mathbf{q}}\rangle\delta_{nn_0}+a_n)/\{(R_0{}^2-R^2(\varepsilon_{n_0}))\langle\varphi|\zeta_{\mathbf{q}}\rangle M\omega\}, \tag{9}$$

which satisfies the *RR*

$$-M\omega R^2(\varepsilon_n)b_n+\hat{Q}b_n=\delta_{nn_0} \tag{10}$$

and depends thus only on the term $T(R)$. The solution of (10) can be easily obtained with a computer by substituting the correct boundary conditions. These conditions depend on the formulation of the problem and will be discussed below. For the time being we shall show that from the known solution of (10) we can determine the cross sections for the inelastic processes.

Let us find the number of electrons having an energy ε_n and passing per unit time through a sphere of sufficiently large radius, in a state

$$|\chi\rangle=a_n\hat{G}^+(\varepsilon_n)|\varphi\rangle\langle\varphi|\hat{G}^+(\varepsilon_n)|\varphi\rangle^{-1}.$$

We have

$$\begin{gathered}\frac{dN(\varepsilon_n)}{dt}=\frac{1}{2i}\int d^2S\left(\chi^*\frac{\partial}{\partial n}\chi-\chi\frac{\partial}{\partial n}\chi^*\right)\\=2\,\mathrm{Im}\int\chi\hat{H}_0\chi^*\,d^3r=-2|a_n|^2\,\mathrm{Im}\langle\varphi|\hat{G}^+|\varphi\rangle^{-1}.\end{gathered} \tag{11}$$

We obtain thus for the cross section of the vibrational transition $n_0\to n$

$$\sigma_{n_0\to n}=\frac{2\beta\,\mathrm{Im}\,R^2(\varepsilon_n)}{k_{n_0}}|a_n|^2,\quad k_{n_0}=(2\varepsilon_{n_0})^{1/2}. \tag{12}$$

Taking into account the connection (9) between a_n and b_n we can get rid in (12) of the parameter β:

$$\sigma_{n_0\to n}=\frac{4\pi}{k_{n_0}{}^2}(M\omega)^2\,\mathrm{Im}\,R^2(\varepsilon_n)\,\mathrm{Im}\,R^2(\varepsilon_{n_0})|b_n|^2. \tag{13}$$

The cross section $\sigma_{n_0\to n_0}$ of the elastic transition is calculated similarly, but in the course of the calculation which must take into account the interference between the electrons scattered by the potential field $V(r)$ and the electrons elastically scattered as the result of the action of the resonant mechanism.

3. We turn now to the *RR* (10). A unique determination of b_n from this system of equations is possible only if two additional conditions are imposed. The first $b_{-1}=0$, is implied in the formulation of the problem. The second condition is connected with the asymptotic behavior of b_n as $n\to\infty$. Next, to investigate the influence of the virtual intermediate state, we specify the model more concretely, putting

$$(\varepsilon^{1/2}+ik_0)^2=M\omega^2\alpha(R_0{}^2-R^2). \tag{14}$$

With decreasing internuclear distance R, the roots of Eq. (14) move in the k plane along the imaginary axis towards each other, and at $R_1=(R_0^2+k_0^2/M\omega^2\alpha)^{1/2}$ the branch corresponding to the bound state as $R\to\infty$ crosses the boundary of the continuous spectrum and goes over to the unphysical energy sheet. At $R=R_0$ the two roots of (14) meet at the point $\varepsilon^{1/2}=-ik_0$, move apart, and form the well known "cross" of the potential-scattering theory. We note that Eq. (14) can be obtained from (3) at

$$V(r)=0,\quad \varphi(r)=(k_0/2\pi)^{1/2}\exp(-k_0r),\quad \beta=M\omega^2\alpha/2. \tag{15}$$

In the case under discussion, the *RR* (10) have as $n\to\infty$ two independent solutions with asymptotics

$$\begin{gathered}b_n{}^\pm\sim n^{-1/4}\exp\{\pm i(n\varphi+\delta n^{1/2}+\gamma\ln n)\}[1+O(n^{-1/2})];\\\cos\varphi=1-1/\alpha,\quad \varphi>0,\quad \delta=2^{1/2}k_0/(2\alpha-1)^{1/2};\\\gamma=[\alpha R_0{}^2-E-k_0{}^2/(2\alpha-1)]/2(2\alpha-1)^{1/2}.\end{gathered} \tag{16}$$

If $\alpha<1/2$, one solution increases exponentially with increasing n and its presence in b_n makes (5) meaningless. Therefore at $\alpha<1/2$ it is necessary to require that the solution of (10) decrease as $n\to\infty$. If, however, $\alpha>1/2$, the two independent solutions of (10) decrease slowly as $n\to\infty$ and it becomes necessary to investigate the problem in greater detail. As shown in the Appendix, a slow decrease of b_n corresponds to a decrease of the term $T(R)$ as $R\to\infty$, i.e., it is due to a new channel that appears in the system, namely the dissociative-attachment (associative-detachment) channel. The following connection exists between the asymptotic form of the solution of (10) as $n\to\infty$:

$$b_n=B_+b_n{}^++B_-b_n{}^-, \tag{17}$$

and the asymptotic wave function of the system as $R\to\infty$:

$$|\Psi(R)\rangle\sim A_+|\Psi_+(R)\rangle+A_-|\Psi_-(R)\rangle, \tag{18}$$

where $|\Psi_\pm\rangle$ describe the quasiclassical motion, as $R\to\infty$, of the system in the bound state:

$$\begin{gathered}|\Psi_\pm(R)\rangle=\left[\beta\frac{dR^2}{d\varepsilon}\right]^{-1/2}[2M(E-T(R))]^{-1/4}\langle\varphi|\hat{G}^+(\varepsilon(R))|\varphi\rangle^{-1}M^{1/2}\\\times\hat{G}^+(\varepsilon(R))|\varphi\rangle\exp\left\{\pm i\int^R dR'[2M(E-T(R'))]^{1/2}\right\}\end{gathered} \tag{19}$$

(the functions $|\Psi_\pm\rangle$ are normalized to a unit flux with respect to the nuclear coordinate and to one particle with respect to the electron coordinate). The correspondence between the coefficients $B_\pm$ and $A_\pm$ is established in the Appendix:

$$|A_\pm|^2=\frac{4\pi}{(2\varepsilon_{n_0})^{1/2}}\frac{(2\alpha-1)^{1/2}}{\alpha}\operatorname{Im}R^2(\varepsilon_{n_0})|B_\mp|^2. \tag{20}$$

Thus, if we consider inelastic scattering of an electron having an energy ε by a molecule in the state n_0, then as $R\to\infty$ the wave function of the system should contain only the outgoing wave $|\Psi_+\rangle$. It is necessary therefore to require for this problem that $B_+=0$. This is in fact the second boundary condition for (10). If, however, the associative-detachment process is considered, we have as $R\to\infty$

$$|\Psi(R)\rangle\sim|\Psi_-(R)\rangle+A_+|\Psi_+(R)\rangle, \tag{21}$$

and it must be assumed in place of (7) that

$$c_n=\tilde{a}_n\hat{G}^+(\varepsilon_n)|\varphi\rangle\langle\varphi|\hat{G}^+(\varepsilon_n)|\varphi\rangle^{-1}.$$

We have then for the coefficients a_n the following *RR*:

$$\hat{Q}\tilde{a}_n=M\omega R^2(\varepsilon_n)\tilde{a}_n. \tag{22}$$

Comparing the behavior of the solution of the *RR* (22) at large n with (19), we obtain the coefficients $B_\pm$ and determine the elastic-scattering probability:

$$|A_+|^2=|B_-/B_+|^2.$$

For the associative-detachment cross section with formation of a molecule in a vibrational state n we have

$$\sigma_n^{as}=\frac{\alpha}{(2\alpha-1)^{1/2}}\operatorname{Im}R^2(\varepsilon_n)M\omega|\tilde{a}_n|^2.$$

4. The model described above was used for a system similar to $e+\text{HCl}$. The model parameters were chosen with allowance for the calculation of the HCl^- term[5] and for the data on dissociative attachment.[15] The results of our calculations are shown in Figs. 1 and 2 and in Table I, which give the parameters α, l, and R_0 of the model and the characteristics of the term of the bound state, viz., the point of its departure to the continuous spectrum R_1, the energy E_1 at this point, reckoned from the ground vibrational state of the molecule, the position $R_{\max}$ of the maximum of the term, and the value of the energy at this maximum, reckoned from the ground vibrational state of the molecule. The values of E_1 and $E_{\max}$ cannot be determined very accurately from the numerical calculation of Ref. 5, which yields $E_1\approx 0.6$ eV and $E_{\max}\approx 0.65$ eV. Comparison of the calculation results with the experimental data and with the calculation results of Ref. 13 suggests that, the rough initial approximation (14) notwithstanding, the model yields relatively good results.

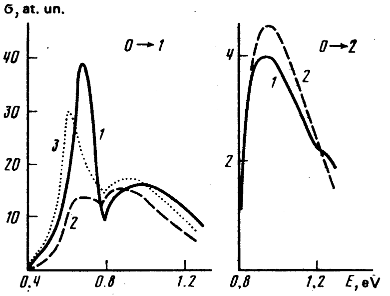

FIG. 1. Cross section for vibrational excitation of the ground vibrational state of a molecule vs the electron energy. The parameters corresponding to the curves are listed in Table I.

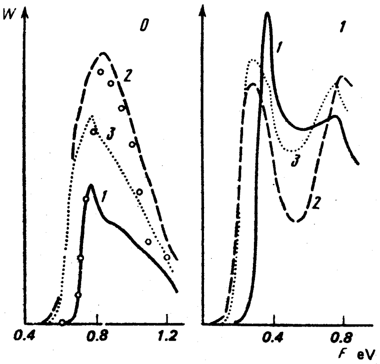

FIG. 2. Probability $|A_+|^2$ (in arbitrary units) of dissociative attachment to the first and ground vibrational levels vs the electron energy. The parameters corresponding to the curves are listed in Table I. The circles show the experimental data of Ref. 15.

APPENDIX

Let us establish the connection between the asymptotic form (17) of the solution of the *RR* (10) and the asymptotic wave function $|\Psi(R)\rangle$ as $R\to\infty$ [Eq. (18)]. We consider the expression $\langle\varphi|\Psi(R)\rangle$, the series (5) for which contains, by virtue of the slow decrease of a_n as $n\to\infty$, a quadratically nonintegrable term. It is easy to verify that to determine the asymptotic form of the considered expression it suffices to investigate the asymptotic behavior of the series

$$u^+(R)=\sum^{\infty} b_n^+\chi_n(R). \tag{A1}$$

Since the error of (16) is such that allowance for it in (A1) replaces u^+ by a quadratically integrable function, the principal term of the asymptotic form of u^+ is determined by the series

$$u^+(R)\sim\exp(-\tilde{R}^2/2)\tilde{R}^{l+1}\sum_{n=0}^{\infty}n^\lambda\exp(i\varphi n+i\delta n^{1/2})L_n^{l+1/2}(\tilde{R}^2),$$

$$\tilde{R}=R(M\omega)^{1/2},\quad \lambda=-3/4+i\gamma-l/2.$$

This series can be summed with the aid of the integral representations

$$\exp(i\delta n^{1/2})=\frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty}\Gamma(s)(-i\delta)^{-s}n^{-s/2}\,ds,$$

$$n^\mu=\frac{1}{\Gamma(-\mu)}\int_1^\infty(\ln u)^{-\mu-1}u^{-n-1}\,du$$

TABLE I.

N	α	l	$k_0\omega^{-1/2}$	$R_0(M\omega)^{1/2}$	$R_1(M\omega)^{1/2}$	E_1, eV	$R_{max}(M\omega)^{1/2}$	E_{max}, eV	ω, eV	M, at. un.
1	0.58	1	0.35	3,25	3.30	0.61	4.60	0,72	0.4	0,98
2	0.58	1	0.15	3,25	3.26	0.58	3,55	0.60	0,4	0,98
3	0.58	1	0.25	3.20	3,23	0,54	3,95	0.61	0.4	0.98

and the formula

$$\sum_{n=0}^{\infty} e^{i\varphi n} u^{-n} L_n^{l+1/2}(\tilde{R}^2) = (1-e^{i\varphi}/u)^{-l-3/2} \exp\left\{\frac{R^2 e^{i\varphi}}{e^{i\varphi}-u}\right\}.$$

In the upshot we obtain

$$u^+(R) = (1-e^{i\varphi})^{-l-3/2} (4\sin^2(\varphi/2))^{-\lambda} \tilde{R}^{-1/2} 2^{1/2}$$
$$\times \exp\left[-i(\tilde{R}^2/2)\operatorname{ctg}(\varphi/2) + i\tilde{R}\delta/2\sin(\varphi/2) + 2i\gamma\ln\tilde{R}\right].$$

This asymptotic form must be compared with the asymptotic form of (19). The comparison leads indeed to Eq. (20).

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