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Nonlocal theory of dissociative electron attachment to H₂ and HF molecules

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We develop a method for calculation of dissociative electron attachment cross sections based on the Fano-Feshbach projection-operator approach. The coupling between the diabatic state and electron continuum is calculated with the inclusion of orthogonality scattering and long-range electron-molecule interaction. The dynamics of nuclear motion in the nonlocal complex potential is treated by semiclassical theory. We apply the theory to the calculation of dissociative attachment to the H₂ and HF molecules. Our results for attachment to ground-state hydrogen molecules and the near-threshold vibrational enhancement of H₂ are essentially the same as previous nonlocal results. However, the shape of the energy dependence of the cross section for attachment to vibrationally excited states of H₂ is slightly different. The calculated value for the total attachment cross section to the ground state of HF is consistent with the little experimental data available; more definite conclusions are difficult because of the approximate nature of the experimental results. The results for the vibrational enhancement are in very good agreement with experiment. [S1050-2947(98)02704-8]

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I. INTRODUCTION

Dissociative attachment (DA) occurs when an electron is captured by a molecular target to form a temporary negative ion that subsequently dissociates into neutral and stable anion fragments. Theoretical descriptions of this process were developed using the projection-operator approach [1,2] and the *R*-matrix approach [3]. The latter is completely equivalent to the projection-operator approach if one uses the single-pole approximation for the *R* matrix [4]. An alternative nonresonant approach was developed on the basis of the zero-range-potential theory [5] and the effective range theory [6].

There are two major difficulties in performing *ab initio* calculations of DA for an arbitrary molecule. First, the electronic part of the problem requires calculations of the width and shift of the negative-ion resonance that appear due to coupling between the diabatic negative-ion state and electron continuum. The first state should be calculated using quantum-chemistry codes, and the second using scattering codes. In most DA calculations performed so far (for a comprehensive review, see Ref. [7]) the width as a function of energy and internuclear distance was parametrized in a convenient analytical form consistent with the threshold laws, and the parameters fitted to experimental data or results of *ab initio* calculations of scattering phase shifts. The second difficulty is related to the complete treatment of the nuclear dynamics. After elimination of the electron coordinates, the problem is reduced to solving the Schrödinger equation with a nonlocal complex potential. The exact treatment of the real part of the nonlocal complex potential presents certain mathematical challenges. Therefore early calculations of DA used local [8] or “partly local” approximations. In the latter case the real part of the nonlocal potential is approximated by a local energy-independent potential [9] or a local energy-dependent potential [10].

The first complete treatment of the nonlocal dynamics was given by Mündel and Domcke [11] for a model problem. Subsequently, low-energy DA for H₂ [12] and HCl [13] were

calculated. In particular, it was found [12] that a completely nonlocal treatment of the nuclear dynamics in the $^2\Sigma_u^+$ resonance of H₂ is essential. In these papers the nonlocal part of the potential is represented in a separable form using the Lanczos basis of the Morse Hamiltonian. An alternative semiclassical approach developed from an earlier similar treatment [14] of the local theory was developed by Kalin and Kazansky [15]. The suitability of this method is a consequence of the small ratio of the electron mass to the mass of the molecule, and allows one to avoid manipulations with rapidly oscillating functions representing highly excited states and the vibrational continuum, which is a part of the procedure employed in Refs. [11–13]. A similar treatment of the nuclear dynamics was proposed [16,17] within the framework of the *R*-matrix theory, and employed in calculations of DA to the HCl [17,18] and HF [19] molecules.

All nonlocal calculations performed so far have been based on a semiempirical or semiphenomenological fit of the resonance width as a function of energy and internuclear distance. The semiclassical approach [15] allows one to proceed with nonlocal calculations in a more straightforward manner. Although the first calculations [15] were performed with a parametrized width, it is possible, in principle, to do the same calculations with the width presented in a numerical form obtained from *ab initio* calculations. In the present paper we develop this procedure and apply it to two simple diatomic molecules, H₂ and HF. These targets present a special interest in terms of applications of the nonlocal theory for two reasons. First, the low-energy DA in these systems is driven by very wide shape resonances, and nonlocal effects become especially important in this situation [7]. Second, the HF molecule possesses a supercritical electric dipole moment; that is, the moment supports an infinite number of HF[−] states, although in practice the stable HF[−] anion does not exist because of rotational motion. This makes a treatment of the nonlocal dynamics especially challenging. The only existing DA calculations [19] for HF involve several approximations, and should be compared with a complete *ab initio* theory. The present paper makes a major step in this

direction. Although we still have several semiempirical adjustments in the present calculations which are discussed below, we develop a procedure which allows us in principle to perform the DA calculations *ab initio* and extend them relatively easily to polyatomic molecules.

It is important to emphasize at this point that the method we use to treat the nonlocal dynamics in this paper works only above the DA threshold. Of course, vibrational excitation processes can occur, and are especially interesting, below the DA threshold. Since the treatment of the vibrational dynamics in this latter case requires a somewhat different approach, this problem will be discussed in a separate paper.

The structure of the present paper is as follows. Section II discusses our treatment of the diabatic state and its interaction with the electron continuum. Section III describes the electron continuum. In particular, we discuss our treatment of the orthogonality scattering and the potential scattering, and how the latter influences the width and shift functions. Section IV summarizes our treatment of the nonlocal vibrational dynamics. In Secs. V and VI we present the DA results for H₂ and HF, respectively. We show that they agree quite well with the existing experimental data and previous nonlocal (for H₂) and *R*-matrix (for HF) calculations.

II. DIABATIC STATE AND ITS INTERACTION WITH THE CONTINUUM

Resonance theory in electron scattering is usually formulated using projection operators to separate the resonance state from the background scattering [20,7]. For the purposes of discussing DA, the resonance state is approximated by a diabatic state that depends upon the internuclear separation as a parameter. This state must be “supported” to prevent variational collapse by a projection onto a restricted portion of Hilbert space, or, more commonly, must be calculated in terms of a fixed finite basis. The calculations reported in this paper use the latter method. The Schrödinger equation

$$H\Psi = E\Psi \quad (1)$$

becomes, when separated,

$$P(E-H)P = PHQ, \quad (2)$$

$$Q(E-H)Q = QHP, \quad (3)$$

where

$$Q = Q^\dagger = Q^2, \quad (4)$$

$$P = I - Q. \quad (5)$$

We symbolize our diabatic state by $|b\rangle = |b(R)\rangle$, an L^2 function normalized to one at all R , and, in terms of this, we set $Q = |b\rangle\langle b|$. In the present work we use for $|b\rangle$ a fixed Gaussian basis wave function of the sort commonly produced by *quantum-chemical* calculations such as GAUSSIAN 92 [21]. What we shall call the primitive continuum wave function is written

$$\Psi(\vec{r}_1 \cdots \vec{r}_{n+1}) = NA \psi(\vec{r}_1 \cdots \vec{r}_n)_g F_E(\vec{r}_{n+1}), \quad (6)$$

where N is a normalization constant, and A is the antisymmetrizer. This must still be subjected to the various projections and modifications described in Sec. III.

In order to use these two functions in our calculations, we need two matrix elements, *viz.* $\langle \Psi | b \rangle$ and $\langle \Psi | H | b \rangle$. They need to be worked out for a number of different energies, and we wish to test our calculations using a number of different assumptions concerning F_E . Furthermore, numerical integrations must be used for at least some of the terms in these matrix elements. All of these considerations led to our developing a procedure in which a relatively simple one-dimensional numerical integration together with a sum over l and m spherical harmonics serves to evaluate the matrix elements.

Specifically, we need to evaluate the integral

$$\begin{aligned} \langle \Psi | H | b \rangle = N \int \psi(\vec{r}_1 \cdots \vec{r}_n)_g F_E(\vec{r}_{n+1}) \\ \times H b(\vec{r}_1 \cdots \vec{r}_{n+1}) d\tau_1 \cdots d\tau_{n+1}, \end{aligned} \quad (7)$$

with a similar expression for $\langle \Psi | b \rangle$. In Eq. (7) it is assumed that b is correctly antisymmetrized and normalized. Now defining

$$H(\vec{r}) = N \int \psi(\vec{r}_1 \cdots \vec{r}_n)_g H b(\vec{r}_1 \cdots \vec{r}_n, \vec{r}) d\tau_1 \cdots d\tau_n, \quad (8)$$

we may obtain $\langle \Psi | H | b \rangle = \int F_E(\vec{r}) H(\vec{r}) d\tau$ with a single three-dimensional integration. A similar procedure serves to evaluate $\langle \Psi | b \rangle$.

When the functions are expressed as multiconfigurational sums over antisymmetrized products, the integral defined in Eq. (8) is an algebraically complicated sum over products of one- and two-electron integrals and individual orbitals. The Slater-Condon [22] rules are somewhat complicated in this case, involving what are the equivalent of three-particle operators. We have found this most easily handled by using the following formalism. Consider a function Ψ_δ that is the same as Ψ itself except that $F_E(\vec{r}_{n+1})$ is replaced by $\delta(\vec{r} - \vec{r}_{n+1})$. In terms of this new function the functions $H(\vec{r})$ and the corresponding quantity we call $O(\vec{r})$ are given by

$$H(\vec{r}) = \langle \Psi_\delta | H | b \rangle, \quad (9)$$

$$O(\vec{r}) = \langle \Psi_\delta | b \rangle, \quad (10)$$

and these quantities depend, otherwise, only upon the internuclear distance. Obtaining the final matrix elements is then only a matter of doing the integrations

$$\langle \Psi | H | b \rangle = \int H(\vec{r}) F_E(\vec{r}) d\tau, \quad (11)$$

$$\langle \Psi | b \rangle = \int O(\vec{r}) F_E(\vec{r}) d\tau. \quad (12)$$

As stated above, these last integrations are actually performed in an lm basis, which is an elementary modification of the Cartesian forms displayed in Eqs. (11) and (12).

TABLE I. Typical values of $H|b\rangle$ and $|b\rangle$ values for three different r values and several l values for H_2 at the equilibrium internuclear separation. It will be recalled that $|b\rangle$ has σ_u symmetry.

l	m	$r=0.36$ a.u.		$r=0.71$ a.u.		$r=1.06$ a.u.	
		$H b\rangle$	$ b\rangle$	$H b\rangle$	$ b\rangle$	$H b\rangle$	$ b\rangle$
1	0	0.014 20	0.054 40	-0.057 69	0.177 93	0.001 10	0.297 91
3	0	-0.013 02	0.001 75	-0.131 09	0.014 26	-0.057 17	0.016 82
5	0	0.004 43	0.000 31	-0.109 82	0.004 60	-0.046 59	0.002 37
7	0	0.002 92	0.000 05	-0.125 75	0.001 87	-0.016 13	0.000 71
9	0	0.000 46	0.000 00	-0.167 38	0.000 51	-0.001 20	0.000 26
11	0	-0.000 56	-0.000 00	-0.198 40	-0.000 19	0.001 91	-0.000 02

The expansion of $\langle b|\Psi\rangle$ and $\langle b|H|\Psi\rangle$ in spherical harmonics was accomplished using a mixed numerical-analytical procedure based upon Lebedev optimal spherical integration formulas [23]. The center of mass was used as the origin of the spherical polar coordinate system for the lm basis expansion.

Table I shows typical values for H_2 at an internuclear distance of 1.4 a.u. We show two values somewhat distant from a nucleus and one close to it. Only the nuclear attraction term causes difficulties, and these occur when a point is near or at a nucleus. Since numerical integration procedures in general require smooth integrands to be useful, a modification of $H|\Psi\rangle$ is required to apply the Lebedev procedure. This we accomplished by subtracting terms that could be evaluated analytically, and that eliminated a sharp cusp in the nuclear attraction terms. The Lebedev procedure could then be applied to this difference, which was subsequently corrected with the analytic formulas for the subtracted terms. It is seen in Table I that, with increasing l , there is a rapid fall-off in magnitude of the quantities. The exception is the set of values of $H|\Psi\rangle$ for a radial distance close to a nuclear radial distance. In spite of this, there is no difficulty; the fall-off in magnitude of higher- l waves in low-energy continuum functions still provides a satisfactory convergence rate.

This general method is valid for $|b\rangle$ and ψ_g functions of any complexity, and we are working on programs that will implement this method for multiconfiguration Gaussian wave functions. The present calculations were performed with single configuration wave functions. Specifically, ψ_g for H_2 was obtained in a split valence basis based upon the results of Huzinaga [24] and for HF a Dunning-Hay basis [25] was used. These same bases were used in each case for the $|b\rangle$ function. In the latter case Koopmans' theorem [26] provides a simple alternative to more complicated stabilization or coordinate rotation methods for obtaining the diabatic state [27]. For both of these molecules we thus use the first virtual orbital from the Hartree-Fock treatment, in addition to the occupied orbitals to form the all electron doublet $|b\rangle$ function. It is well known that the use of bases with too great a flexibility will result in a variational collapse of the virtual orbitals. The bases here have proved able to give a good account of both the neutral molecule and quasi-bound state functions like $|b\rangle$.

It is, perhaps, not out of place to comment that, in principle, the results from the Feshbach projection procedure should be completely independent of the specific details of the Q operator. In practice, real calculations will not behave

so well, but as methods approach the ideal, we expect the results to be usefully insensitive to our exact Q .

III. POTENTIAL AND ORTHOGONALITY SCATTERING

A. Equation for the continuum state

The basic function with which we start our calculations of nuclear dynamics is the matrix element describing the interaction between the diabatic state $|b\rangle$ and the continuum state $|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle$ (Ref. [7]),

$$V_{b\mathbf{k}} = \langle b|H_{\text{el}}|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle. \quad (13)$$

Here $|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle$ is the solution of the projected Lippman-Schwinger equation

$$|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle = |\hat{\mathbf{k}}^{(+)}\rangle + \hat{G}_0^{(+)}V_{\text{opt}}|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle, \quad (14)$$

where V_{opt} is the optical potential describing the electron-molecule interaction including the exchange and polarization effects, and $|\hat{\mathbf{k}}^{(+)}\rangle$ and $\hat{G}_0^{(+)}$ are given by the equations

$$|\hat{\mathbf{k}}^{(+)}\rangle = |\mathbf{k}\rangle - G_0^{(+)}|b\rangle\langle b|G_0^{(+)}|b\rangle^{-1}\langle b|\mathbf{k}\rangle, \quad (15)$$

$$\hat{G}_0^{(+)} = G_0^{(+)} - G_0^{(+)}|b\rangle\langle b|G_0^{(+)}|b\rangle^{-1}\langle b|G_0^{(+)}|. \quad (16)$$

Here $|\mathbf{k}\rangle$ is a plane wave and $G_0^{(+)}$ is the free-particle Green's function corresponding to the outgoing-wave boundary condition, $G_0^{(+)} = (E + i0 - H_0)^{-1}$. Equations (15) and (16) provide the orthogonality of the continuum state to the diabatic state $|b\rangle$ required in the case of a shape resonance. Combining these equations, we obtain

$$\begin{aligned} |\hat{\phi}_{\mathbf{k}}^{(+)}\rangle &= |\hat{\mathbf{k}}^{(+)}\rangle + G_0^{(+)}V_{\text{opt}}|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle \\ &\quad - G_0^{(+)}|b\rangle\langle b|G_0^{(+)}|b\rangle^{-1}\langle b|G_0^{(+)}V_{\text{opt}}|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle. \end{aligned} \quad (17)$$

In order to solve this equation, Domcke [28] suggested the use of a separable expansion for V_{opt} , and this procedure was implemented in several DA calculations [11–13]. Since we are interested in the long-range effects in $V_{b\mathbf{k}}$, and the separable approximation does not work well for long-range potentials, we use a different approach. By acting with the operator $E - H_0$ on both sides of Eq. (17), we convert it into an inhomogeneous integrodifferential equation

$$(H_0 + V_{\text{opt}} - E)|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle = |b\rangle\langle b|G_0^{(+)}|b\rangle^{-1}(\langle b|\mathbf{k}\rangle + \langle b|G_0^{(+)}V_{\text{opt}}|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle). \quad (18)$$

The solution of this equation can be presented in the form

$$|\hat{\phi}_{\mathbf{k}}^{(+)}\rangle = |\phi_{\mathbf{k}}^{(0)}\rangle + a_{\mathbf{k}}|\phi^{(1)}\rangle, \quad (19)$$

where $a_{\mathbf{k}}$ is a constant, and $|\phi_{\mathbf{k}}^{(0)}\rangle$ and $|\phi^{(1)}\rangle$ satisfy the following differential equations:

$$(H_0 + V_{\text{opt}} - E)|\phi_{\mathbf{k}}^{(0)}\rangle = 0, \quad (20)$$

$$(H_0 + V_{\text{opt}} - E)|\phi^{(1)}\rangle = |b\rangle, \quad (21)$$

where the outgoing-wave boundary conditions still hold for both $|\phi_{\mathbf{k}}^{(0)}\rangle$ and $|\phi^{(1)}\rangle$. Substituting Eq. (19) into Eq. (17), and noticing that the integral equations for $|\phi_{\mathbf{k}}^{(0)}\rangle$ and $|\phi^{(1)}\rangle$ are

$$|\phi_{\mathbf{k}}^{(0)}\rangle = |\mathbf{k}\rangle + G_0 V_{\text{opt}}|\phi_{\mathbf{k}}^{(0)}\rangle, \quad (22)$$

$$|\phi^{(1)}\rangle = -G_0|b\rangle + G_0 V_{\text{opt}}|\phi^{(1)}\rangle, \quad (23)$$

we obtain

$$a_{\mathbf{k}} = -\langle b|\phi^{(1)}\rangle^{-1}\langle b|\phi_{\mathbf{k}}^{(0)}\rangle. \quad (24)$$

The problem is reduced to the numerical integration of the differential equations (20) and (21).

B. Electron-molecule interaction in the continuum

There are many methods for calculating continuum states for electron-molecule scattering, taking into account electron exchange and short-range correlation effects at different levels of approximations (see Ref. [29] and references therein). Most of them are based on a single-center expansion of the continuum wave function in spherical harmonics [30]. Numerical realizations of this method alternative to that of direct numerical integration are the complex Kohn variational method [31] and the linear algebraic method [32]. An important feature of the projection-operator approach is that after calculation of this state we ‘‘project out’’ a substantial part of the short-correlation effects due to imposing the orthogonality of the continuum state to the bound state. As a result the background part (or nonresonant part) of the scattering phase shift is virtually unaffected by short-range correlation effects. The previous analysis of the electron scattering by H_2 molecule [33] shows that in the low-energy region the potential scattering contribution to the phase shift is almost negligible as compared to the orthogonality scattering. This means that even the long-range polarization effect is not important in this case, due to the low value of polarizability of the H_2 molecule. However, the case of polar and/or highly polarizable targets is different, since the coupling between the diabatic state and the continuum state becomes strongly energy dependent at low electron energies.

Based on these observations, in the present work for calculations of $|\phi_{\mathbf{k}}^{(0)}\rangle$ we use the plane-wave approximation for H_2 , and include the long-range interaction for HF. In the latter case we use the model potential employed in our pre-

vious rotational close-coupling calculations [34]

$$V_{\text{opt}}(\mathbf{r}) = -\frac{D \cos\theta}{r^2} \left[1 - \exp\left\{ -\left(\frac{r}{r_d}\right)^3 \right\} \right] - \frac{QP_2(\cos\theta)}{r^3} \left[1 - \exp\left\{ -\left(\frac{r}{r_q}\right)^4 \right\} \right] - \frac{\alpha_0 + \alpha_2 P_2(\cos\theta)}{2(r^2 + r_p^2)^2}, \quad (25)$$

where D is the molecular dipole moment, Q is the quadrupole moment (calculated in the center-of-mass reference frame), θ is the angle between the electron radius vector and the molecular axis, and α_0 and α_2 are, respectively, the isotropic and anisotropic parts of the fixed nuclei polarizability. The parameters r_p , r_d , and r_q were fitted in Ref. [34] to reproduce experimentally observed rates for ionization of Rydberg atoms in their collisions with the HF molecules. This semiempirical choice of cutoff parameters was employed in earlier work [35] on electron-molecule scattering. The DA cross sections calculated in the present paper are very insensitive to the values of these parameters, and here they serve just to remove the nonphysical singularities at the origin by a reasonable choice of the cutoff parameters. In fact, as we show later, the DA cross sections do not change substantially if we omit the quadrupole and the polarization parts of the interaction potential.

We should emphasize that the present approach, which ignores the short-range interaction for the continuum state, is justified for calculations of cross sections of resonance processes, such as DA and resonant vibrational excitation, and does not require great computational effort in the continuum-state part of the problem. On the other hand, this approach would be invalid for the calculation of elastic scattering.

C. Integration of equations for the continuum state

We now discuss the method of numerical integration of Eqs. (20) and (21). If $V_{\text{opt}} = 0$, as we assume in the hydrogen case, then $|\phi_{\mathbf{k}}^{(0)}\rangle$ is simply the plane wave, and $|\phi^{(1)}\rangle$ is obtained by integrating the product of the free-particle Green’s function G_0 and the diabatic function $|b\rangle$. Using the Gaussian basis, we can express the results as a sum of the error functions with a complex argument. If V_{opt} is nonzero, we start with the standard partial-wave expansion for our bound and continuum wave functions in the coordinate representation in the body frame,

$$\phi_{\mathbf{k}}^{(0)}(\mathbf{r}) = 4\pi \sum_{l'l'm} i^{l'} Y_{l'm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}}) \frac{u_{l'l'}^{m}(r)}{r}, \quad (26)$$

$$\phi^{(1)}(\mathbf{r}) = \sum_l Y_{lm_r}(\hat{\mathbf{r}}) \frac{u_l^{(1)}(r)}{r}, \quad (27)$$

$$|b\rangle = \sum_l Y_{lm_r}(\hat{\mathbf{r}}) \frac{\chi_l(r)}{r}, \quad (28)$$

where m_r is the projection of the electron angular momentum for the resonant state. (We assume cylindrical symmetry.) Functions $u_{ll'}(r)$ and $u_l^{(1)}(r)$ satisfy the asymptotic conditions

$$u_{ll'}^m(r) \sim e^{-ikr} \delta_{ll'} - e^{ikr} S_{ll'}, \quad (29)$$

$$u_l^{(1)}(r) \sim S_l^{(o)} e^{ikr}, \quad (30)$$

where $S_{ll'}$ are the S -matrix elements for the potential scattering, and the complex numbers $S_l^{(o)}$ can be related to the matrix elements for the orthogonality scattering. We obtain the standard system of coupled equations for the radial functions $u_l^{(1)}(r)$

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \right] u_l^{(1)}(r) - 2 \sum_{l'} U_{ll'}(r) u_{l'}^{(1)}(r) = -2\chi_l(r), \quad (31)$$

where $U_{ll'}(r)$ are the matrix elements of the optical potential V_{opt} , and a similar, but homogeneous, system for $u_{ll'}^m(r)$.

Whereas the methods of numerical integration of homogeneous systems are well known and could be applied in our case, a direct numerical integration of the inhomogeneous system (31) leads to very strong instabilities at higher angular momenta ($l > 3$) that are related to the behavior of the singular solution of the homogeneous equation near the origin (see Appendix A). Therefore we have chosen the Green's-function method to solve Eqs. (31). Let us write this system of equations in the following compact matrix form

$$u'' + qu = s, \quad (32)$$

where \prime means the derivative in $\rho = kr$, q is a square matrix, and s and u are columns. We have the boundary conditions

$$u \rightarrow 0 \quad \text{as} \quad \rho \rightarrow 0, \quad u \rightarrow e^{i\rho l} \quad \text{as} \quad \rho \rightarrow \infty, \quad (33)$$

where $\rho_l = \rho - l\pi/2$. Introducing the regular $u^{(r)}$ and irregular $u^{(\pm)}$ solutions of the homogeneous equation with the asymptotic behavior as $\rho \rightarrow \infty$,

$$u^{(\pm)} \sim e^{\pm i\rho l}, \quad u^{(r)} \sim e^{-i\rho l} - e^{i\rho l} S, \quad (34)$$

where S is the potential scattering matrix. $u^{(r)}$ and $u^{(\pm)}$ are square matrices with different columns corresponding to different linearly independent solutions.

These solutions have the following properties proven in Appendix B:

$$u^{(r)} u^{(+T)} = u^{(+)} u^{(r)T}, \quad (35)$$

$$\{u^{(+)}\}' u^{(r)T} - \{u^{(r)}\}' u^{(+T)} = 2iI, \quad (36)$$

where the superscript T denotes the transposition, and I is the unit matrix. It is easy to verify now by direct substitution that the solution of Eq. (32) with the boundary conditions (33) can be written as

$$u = \frac{1}{2i} \left\{ u^{(r)}(\rho) \int_{\rho}^{\infty} u^{(+T)}(\rho') s(\rho') d\rho' + u^{(+)}(\rho) \int_0^{\rho} u^{(r)T}(\rho') s(\rho') d\rho' \right\}, \quad (37)$$

which is an apparent generalization of a similar statement for a single differential equation. The problem is now reduced to an integration of the homogeneous equation with subsequent calculations of numerical quadratures in Eq. (37).

IV. NUCLEAR DYNAMICS

The wave function $|\Psi_{\mathbf{k},E}\rangle$, describing the nuclear motion in the dissociating channel, satisfies outgoing-wave boundary conditions and depends on the total energy of the system E and the electron momentum \mathbf{k}_i in the initial channel. The Schrödinger equation for this function has the form [7]

$$(E - H_d) |\Psi_{\mathbf{k},E}\rangle - F |\Psi_{\mathbf{k},E}\rangle = V_{b\mathbf{k}_i} |v_i\rangle, \quad (38)$$

where H_d is the Hamiltonian for the nuclear motion in the diabatic potential $V_d(R)$, $|v_i\rangle$ is the initial state of the neutral molecule, and F is the nonlocal complex potential

$$F = \int k dk d\hat{\mathbf{k}} V_{b\mathbf{k}} G_n^{(+)} \left(E - \frac{1}{2} k^2 \right) V_{b\mathbf{k}}^*, \quad (39)$$

where $G_n^{(+)}(E)$ is the Green's operator for the nuclear motion in the potential of the neutral molecule $V_0(R)$. The Lippman-Schwinger form of Eq. (38) is

$$|\Psi_{\mathbf{k},E}\rangle = G_d^{(+)}(E) (V_{b\mathbf{k}_i} |v_i\rangle + F |\Psi_{\mathbf{k},E}\rangle), \quad (40)$$

where $G_d^{(+)}(E) = (E + i0 - H_d)^{-1}$. We expand $|\Psi_{\mathbf{k},E}\rangle$ in the eigenstates $|v\rangle$ of the Hamiltonian for the neutral molecule

$$|\Psi_{\mathbf{k},E}\rangle = \sum_v b_{v\mathbf{k}_i} |v\rangle, \quad (41)$$

where the symbol \sum_f means the sum over all discrete vibrational states and integration over the vibrational continuum. Using the spectral representation for $G_n^{(+)}$ we obtain the following equation for $b_{v\mathbf{k}_i}$:

$$b_{v\mathbf{k}_i} = \langle v | G_d^{(+)}(E) V_{b\mathbf{k}_i} |v_i\rangle + \sum_{v'} \int k dk d\hat{\mathbf{k}} \frac{\langle v | G_d^{(+)}(E) V_{b\mathbf{k}} |v'\rangle \langle v' | V_{b\mathbf{k}}^* |\Psi_{\mathbf{k},E}\rangle}{E + i0 - \frac{1}{2} k^2 - \epsilon_{v'}}, \quad (42)$$

where ϵ_v are eigenenergies of the neutral molecule.

The following treatment of the vibrational dynamics is based on the semiclassical approach of Kalin and Kazansky [15], although we use a slightly different notation more consistent with that of Domcke [7]. We evaluate all matrix elements of Eq. (42) in the coordinate representation and assume that the main contribution is given by the Franck-Condon point R_v defined by the equation

$$\epsilon_v - V_0(R_v) = E - V_d(R_v). \quad (43)$$

(Note that R_v also depends on the total energy E .) The capture amplitude $V_{b\mathbf{k}}$ is weakly dependent on the internuclear distance R , and therefore can be factored out from all integrals over R . In particular,

$$\langle v | G_d^{(+)}(E) V_{b\mathbf{k}} | v' \rangle = V_{b\mathbf{k}}(R_{v'}) \langle v | G_d^{(+)}(E) | v' \rangle, \quad (44)$$

$$\langle v' | V_{b\mathbf{k}}^* | \Psi_{\mathbf{k};E} \rangle = V_{b\mathbf{k}}^*(R_{v'}) \langle v' | \Psi_{\mathbf{k};E} \rangle. \quad (45)$$

The integral equation for $b_{v\mathbf{k}_i}$ can be rewritten now in the closed form

$$b_{v\mathbf{k}_i} - \sum_{v'} \langle v | G_d^{(+)}(E) | v' \rangle F_{v'} b_{v'\mathbf{k}_i} = V_{b\mathbf{k}_i}(R_{v_i}) Q_{v_i v}, \quad (46)$$

where

$$Q_{v_i v} = \langle v | G_d^{(+)}(E) | v_i \rangle \quad (47)$$

and

$$F_v = \int k dk d\hat{\mathbf{k}} \frac{|V_{b\mathbf{k}}(R_v)|^2}{E + i0 - \epsilon_v - \frac{1}{2}k^2} \quad (48)$$

are the diagonal elements, taken at the Franck-Condon point, of the kernel of the nonlocal complex potential F [Eq. (39)]. They are related to the partial resonance widths Γ_v and shifts Δ_v in the usual way:

$$F_v = \Delta_v - \frac{i}{2} \Gamma_v. \quad (49)$$

Equation (46) represents the basic integral equation of the semiclassical nonlocal theory [15]. It is convenient first to eliminate the dependence on \mathbf{k}_i using the substitution

$$b_{v\mathbf{k}_i} = V_{b\mathbf{k}_i}(R_{v_i}) a_v, \quad (50)$$

which leads to the equation

$$a_v - \sum_{v'} \langle v | G_d^{(+)}(E) | v' \rangle F_{v'} a_{v'} = Q_{v_i v}. \quad (51)$$

Now we will briefly summarize the algorithm for its solution referring the reader for more details to the original paper by Kalin and Kazansky [15].

First we calculate the matrix elements of the Green's function using the quasiclassical representation for the nuclear wave functions and the stationary phase method. The major contribution to the integrals is given by the Franck-Condon point [Eq. (43)]. If this point lies close to the classical turning point, the result should be modified using the Airy function, as discussed in Refs. [14,36,37]. As a result, one obtains a quasiseparable representation for $\langle v | G_d^{(+)}(E) | v' \rangle$ [15]. Equation (51) can then be solved recursively in the region of the discrete spectrum. The solution is expressed as a linear function of an unknown parameter depending on the solution in the region of vibrational con-

tinuum. This parameter is determined from the matching with the continuum function having the proper asymptotic behavior. The DA cross section is expressed then through the resulting solution for a_v .

V. SOME COMPUTATIONAL DETAILS

As discussed in Sec. II, in this paper we calculate the diabatic state using a single-configuration Hartree-Fock wave function. Although, as we will show below, this approach in general gives rather good results for the DA cross sections, it creates two problems in the limit of large internuclear distances, $R \rightarrow \infty$. First, the negative-ion energy is not the eigenenergy of the electronic Hamiltonian, and this leads to a shifted DA threshold. Second, the diabatic state is not the eigenstate of the Hamiltonian, and this leads to a nonzero coupling between the diabatic state and continuum in the limit $R \rightarrow \infty$. To correct these drawbacks of the single-configuration approximation, we make two adjustments. First, we shift our negative-ion curves uniformly (by -0.54 eV for H_2 and by -0.86 eV for HF) in order to obtain the experimentally observed DA threshold. Second, we extrapolate our calculated width Γ and shift Δ to large internuclear distances forcing them to approach 0 at $R \rightarrow \infty$. With our basis, the correction to the B^- wave function due to the presence of a neutral atom A decays as a Gaussian function. Therefore the coupling parameter $V_{b\mathbf{k}}$ decays as $\exp(-\eta R^2)$, where $\eta = 0.1233$ is the smallest exponent used in our basis. Therefore the width

$$\Gamma(E, R) = 2\pi \int d\hat{\mathbf{k}} |V_{b\mathbf{k}}|^2 \quad (52)$$

at large R can be parametrized as

$$\Gamma(E, R) = b(E) \exp\{-2\eta[R - R_0(E)]^2\}, \quad (53)$$

where $b(E)$ and $R_0(E)$ are adjustable parameters. Since our calculated width does not approach 0 at $R \rightarrow \infty$, the parametrization (53) creates a certain nonanalyticity in Γ as a function of R . This leads to small uncertainties in the DA cross sections in a narrow region close to the threshold, which will be discussed in Sec. VI.

Another computational detail has to do with the threshold behavior of Γ as a function of energy E . In the absence of the long-range dipolar interaction it behaves, according to the Wigner law, as $E^{3/2}$ for the $\text{H}_2^- (^2\Sigma_u^+)$ resonance and as $E^{1/2}$ for the $\text{HF}^- (\Sigma)$ resonance. However, HF possesses a permanent dipole moment D , and the threshold law should be modified. If $D < D_{\text{cr}} = 0.6395$ a.u., then [38]

$$\Gamma(E) = \text{const} \times E^\beta, \quad (54)$$

where β depends only on the dipole moment D , and approaches 0 when $D \rightarrow D_{\text{cr}}$. If $D > D_{\text{cr}}$, then [38]

$$\Gamma(E) = \frac{\text{const}}{1 + e^{2\pi\mu} + 2e^{\pi\mu} \cos(\mu \ln E + \gamma)}, \quad (55)$$

where μ depends only on D , and γ depends both on D and the short-range interaction. For the equilibrium internuclear separation in HF $\mu = 0.261$.

TABLE II. Potential-curve parameters in a.u.

	A	α	B	D	β
H ₂	0.1764	1.0813	0.030 97	0.1466	1.6302
HF	0.2252	1.1735	0.033 07	0.1002	1.8638

Although $\Gamma(E)$ formally exhibits an infinite number of oscillations as $E \rightarrow 0$, for molecules with a moderate dipole moment, like HF, these oscillations occur within a very narrow energy region that is usually narrower than the rotational constant. The theory should be modified in this region [39], and, as a result, no oscillations are found in either inelastic cross sections or the resonance width. Instead, the width rises sharply from zero at $E=0$ to a finite value, within the energy region corresponding to the rotational spacing. Since we are not interested in this paper in fine-structure effects associated with the rotational motion, we simply assume that Γ is finite at $E=0$, and obtain $\Gamma(0)$ by linear extrapolation. In this case the shift $\Delta(E)$ becomes formally logarithmically divergent at $E \rightarrow 0$. We have found, however, that this singularity is weak enough not to affect our results for the cross sections if we, again, are not interested in a very high-energy resolution. In practice this means that we can calculate $\Delta(E)$ for any non-zero E without having instabilities, and obtain $\Delta(0)$ by interpolating between two values corresponding to two close positive and negative energies.

Finally we should mention that in the present calculations the potential-energy curves $V_0(R)$ and $V_d(R)$ were parametrized in the form of the Morse potentials

$$V_0(R) = A(e^{\alpha(R-R_e)} - 1)^2, \quad (56)$$

$$V_d(R) = B e^{-2\beta R} + D, \quad (57)$$

where R_e is the equilibrium internuclear distance. Parameters entering Eqs. (56) and (57) are given in Table II for the H₂ and HF molecules.

The potential-energy curves for the ground states of H₂ and HF are known with high accuracy. For H₂, *ab initio* data of Kolos and Wolniewicz [40] were used to obtain V_0 , and Morse parameters were calculated by a least-square fit. For HF, parameters were determined from the experimental dissociation energy, vibrational frequency, and equilibrium internuclear distance of Herzberg [41].

We obtained the parameters in V_d in three steps. First, we calculated the energies of the negative ion states relative to the molecular ground states at several internuclear distances by the single-configuration Hartree-Fock method. We then added them to the corresponding neutral curves, and fitted the resultant potential to Morse form. Finally we shifted the potentials to have the correct electron affinities of H⁻ and F⁻ at infinity.

It should be stressed that the semiclassical theory of dissociative attachment, in contrast to the Lanczos-basis approach [11,12], does not require parametrization of the potential curves, and the functions $\Gamma(E,R)$ and $\Delta(E,R)$. On the other hand, the Morse parametrization allows us to perform computations conveniently.

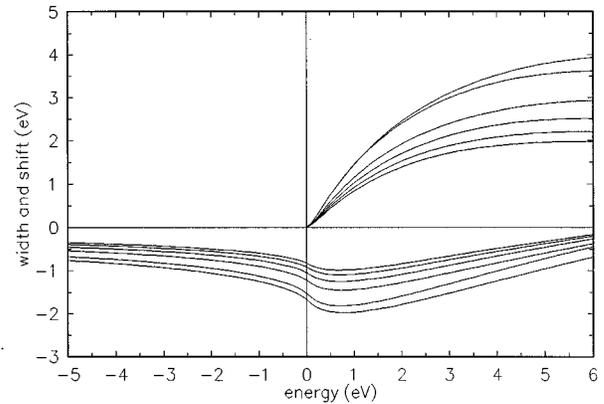


FIG. 1. Calculated width (upper curves) and shift (lower curves) functions for H₂. From top to bottom (bottom to top) the curves for the width (shift) correspond to the internuclear distances $R=1.4, 1.6, 1.8, 2.0, 2.2,$ and 2.4 a.u.

VI. RESULTS FOR THE H₂ MOLECULE

In Fig. 1 we present the width Γ and shift Δ as functions of energy E for several internuclear distances R . The curve shapes and the numerical values are very close to those of Ref. [12]. This means that the approximations employed in the present calculations, namely, the single-configuration approximation for the diabatic state $|b\rangle$ and neglect of the potential scattering for H₂ are not severe, and give a good description of the low-energy Σ_u^+ resonance in H₂⁻. This conclusion is confirmed by our DA calculations for H₂ in its ground state $v=0$, presented in Fig. 2 together with the experimental results [42] and previous nonlocal results [12]. In addition to the equivalence of two calculations in their electronic-structure part, we observe their equivalence in the nuclear-dynamics part; that is, our semiclassical approach gives the same results for attachment to H₂($v=0$) as the Lanczos-basis approach of Ref. [12].

However, for higher vibrational states our results are slightly different. Whereas our threshold peak values for DA to H₂(v) are basically the same as those of Ref. [12], our cross sections as functions of E for $v \geq 2$ vary relatively slowly in the region between 3 and 4.5 eV. This behavior is

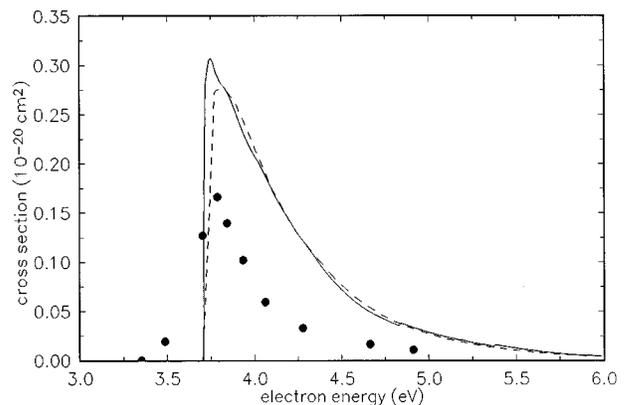


FIG. 2. Dissociative attachment from the vibrational ground state of H₂. Solid curve, present results; dashed curve, nonlocal calculations [12]; circles, experimental data [42].

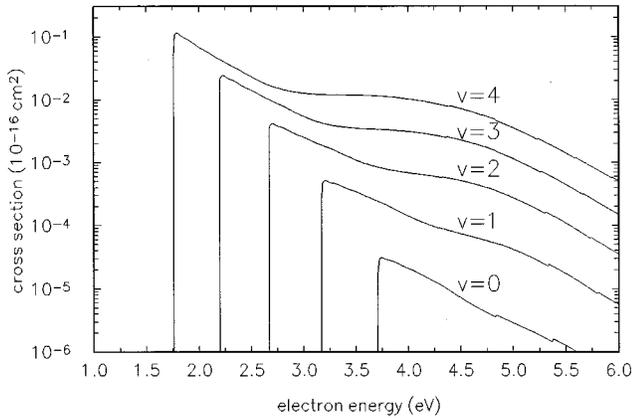


FIG. 3. Dissociative attachment cross sections for various vibrational states of H_2 .

demonstrated in Fig. 3. The relatively stable production of H^- in this region can be explained in the following way. The Franck-Condon points determined by Eq. (43) stay well within the classically allowed region for the nuclear motion in H_2 , which makes the Franck-Condon overlaps and the capture cross section relatively large. At the same time the kinetic energy of the nuclei at the Franck-Condon point is also relatively high (about 1.5–2.0 eV) in this energy region; therefore the survival probability does not drop as fast with growing energy. This peculiar behavior was not observed in the earlier local calculations [43], and is not seen in the $v=2$ results of the nonlocal calculations [12]. In the latter work the authors did not go to higher v . It would be interesting if an experimental verification of this observed feature were possible. The existing experimental data [44] on the vibrational enhancement of DA to H_2 , obtained from measuring the temperature dependence of the cross sections, are inconclusive about the energy dependence of the DA cross sections for higher v .

Another feature of our cross sections is a set of small jumps at certain energies (e.g., at $E=4.8$ and 5.4 eV for $v=0$). These irregularities are caused by a small inaccuracy of the quasiclassical approximation, occurring when we switch the quasiclassical phase integral from being calculated relative to the right turning point to being calculated relative to the left turning point. It should be stressed that even for the lightest molecule, H_2 , this inaccuracy is very small, and it becomes unnoticeable for heavier molecules, particularly HF.

Our results on vibrational enhancement at the thresholds are quite close to those of the other nonlocal calculations [12], and are therefore somewhat below the experimental values [44]. The disagreement increases with growing v , and perhaps can be attributed to the rotational motion, which was included neither in the calculations of Ref. [12] nor in ours. The rotational analysis performed by Wadehra and Bardsley [43] suggests that rotationally excited H_2 molecules have increased attachment cross section at each electron energy.

VII. RESULTS FOR THE HF MOLECULE

In Fig. 4 we present the width and shift functions obtained with the long-range potential (25). As we discussed above,

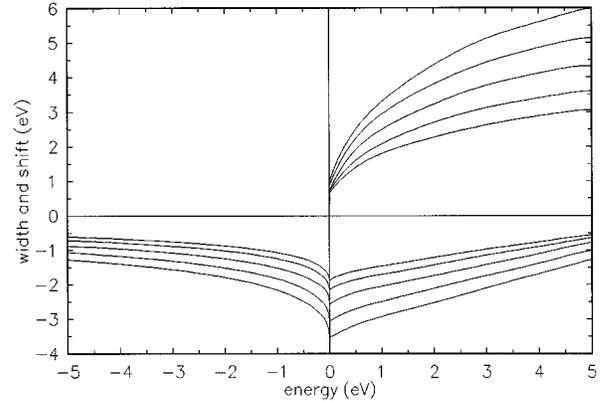


FIG. 4. Calculated width (upper curves) and shift (lower curves) functions for HF. From top to bottom (bottom to top) the curves for the width (shift) correspond to the internuclear distances $R=1.6, 1.8, 2.0, 2.2,$ and 2.4 a.u.

the width function starts with the finite value at $E=0$ due to the dipolar interaction, and the shift function formally has a logarithmic singularity at $E=0$ which we simply ignore by calculating $\Delta(E_0)$ instead of $\Delta(0)$, where E_0 is of the order of magnitude of the rotational spacing. To find out how the long-range interaction affects the DA cross sections, we performed two additional calculations, one with a plane-wave continuum state and the other with a continuum state that includes only dipolar interaction. In Fig. 5 we compare three sets of Γ and Δ for the equilibrium internuclear distance. The plane-wave results give the Wigner law $E^{1/2}$ for Γ . For a stronger interaction the width is higher for the whole investigated range of E and R . Therefore we should expect a smaller DA cross section for a stronger interaction in the continuum.

This is confirmed by our DA calculations presented in Fig. 6. The DA cross sections drop substantially after inclusion of the long-range interaction, but the difference between the two calculations, including the pure dipolar potential and the full potential of Eq. (25), is relatively small.

Two features observed in Fig. 6 should be discussed. The

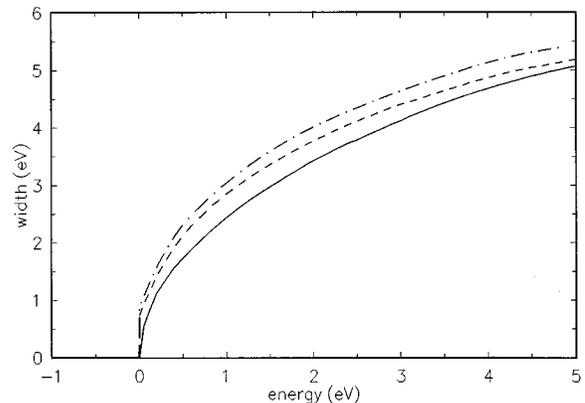


FIG. 5. Comparison of the width function for the equilibrium internuclear separation calculated using various models for the e -HF interaction. Solid curve, the plane-wave approximation; dashed curve, only dipolar interaction included; dot-dashed curve, the full potential [Eq. (25)] included.

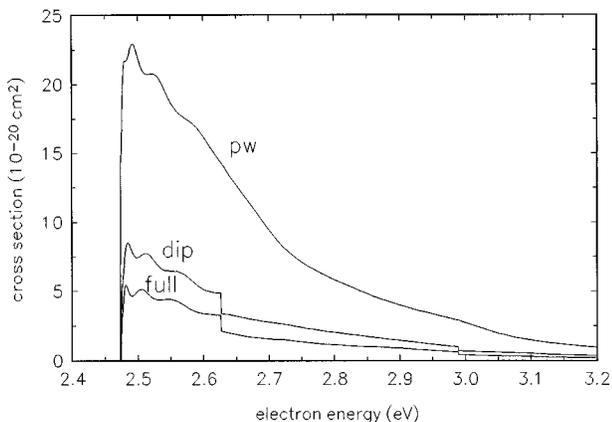


FIG. 6. Dissociative attachment from the vibrational ground state of HF. Curve *pw*, the plane-wave approximation; curve *dip*, only dipolar interaction included; curve *full*, the full potential [Eq. (25)] included.

first is small-amplitude oscillations of the cross sections near the DA threshold. These are related to the inaccuracy of our coupling parameter at large internuclear distances discussed in Sec. V. To confirm this, we varied the parameter η in the extrapolation Eq. (53) within broad limits, and found that the averaged cross section remains the same but the positions of maxima and minima change substantially. This creates a 5% uncertainty in our cross sections in the near-threshold region between 2.48 and 2.55 eV, but realistic values of the DA cross sections could be obtained simply by averaging these spurious oscillations.

The other feature of the cross sections is their sudden drop at the vibrational excitation thresholds, $v=5$ and 6 in the investigated energy region. This result is physical, and is explained by the sudden drops of the negative-ion survival probabilities at the vibrational excitation thresholds which were previously observed in DA of HCl [45]. Note that these drops are not seen in the plane-wave results nor in the DA results for H_2 . This happens because Γ grows much slower in this case, and does not create such noticeably sharp changes in the survival probability.

In Fig. 7 we present our results, including the full long-range interaction, and their comparison with the experimental data [46]. For this purpose we average our results over the energy distribution assuming a Gaussian profile of full width 0.09 eV. After this averaging the stepwise structure at the vibrational thresholds almost disappears, although one can see some indication of it correlating with the experimental data. The experimental cross sections are normalized to the estimated peak value of $2 \times 10^{-20} \text{ cm}^2$. It decreases with energy much more slowly than the theoretical results, indicating perhaps another negative-ion resonance contributing to the DA cross section at higher energy. The experimental threshold for DA is somewhat shifted toward lower energies due to the effects of rotational motion [46], which are not included in the present calculations. According to the results of Teillet-Billy and Gauyacq [6] for HCl molecule, obtained by the effective-range theory, the cross sections depend very weakly on the rotational quantum number J at a given impact energy (in contrast with calculations [43] for H_2). However, rotationally excited molecules have a lower DA threshold, and this makes the DA peak not as sharp as that

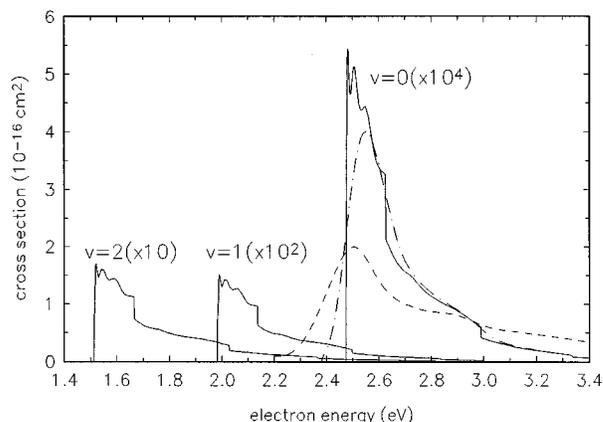


FIG. 7. Dissociative attachment for various vibrational states of HF. Solid curves, present results; dashed curve, experimental data [46] normalized to $2 \times 10^{-20} \text{ cm}^2$ at the peak; dot-dashed curve, present theory averaged over an energy distribution of the width 0.09 eV.

calculated for nonrotating molecules.

The present cross sections are similar to but somewhat higher than those from the previous nonlocal calculations [19], performed within the framework of the resonance R -matrix theory [17]. It is likely that the previous calculations overestimate the long-range interaction by choosing too small a value of the R -matrix radius. In Fig. 7 we also give DA cross sections for higher vibrational states. As in the case of H_2 , we observe a very strong growth of DA with v . In Table III we present the theoretical results for this effect, and compare them with the experimental data of Allan and Wong [47]. The present results agree better with the experiment than the R -matrix calculations [19].

VIII. CONCLUSIONS

We presented a method that allows us to obtain, in a systematic way, DA cross sections for any diatomic molecule and extend it, without principle difficulties, to polyatomic molecules. An important feature of our approach is that it incorporates a full treatment of nuclear dynamics in nonlocal complex potentials and, therefore, is applicable to calculations of DA processes driven by wide resonances when the local and partly local approximations fail. Furthermore, our approach is not as model dependent as previous studies of nonlocal dynamics [12,13], and can clearly be applied to molecules with supercritical dipole moments.

In addition to this, our calculations include several modes in the expansion of the coupling parameter in partial waves, and do not assume single-mode dominance like previous nonlocal calculations [13,15] and resonance R -matrix calcu-

TABLE III. Vibrational enhancement in the threshold DA cross section for HF.

	Present	Theory [19]	Expt. [47]
$\sigma_{v=1}/\sigma_{v=0}$	28	38	21
$\sigma_{v=2}/\sigma_{v=0}$	315	566	300
$\sigma_{v=3}/\sigma_{v=0}$	2019	4484	

lations [19]. This should improve our results for differential dissociative attachment and vibrational excitation cross sections compared to those from single-angular-mode calculations [19]. Another advantage of the present formalism compared to the resonance R -matrix approach [17–19] is that we do not need an additional fitting procedure to reproduce *ab initio* results for eigenphases.

Our calculations for DA to H_2 , and their agreement with previous nonlocal results [12], demonstrate the reliability of the single-configuration approach for a calculation of $|b\rangle$, and the insignificance of the potential scattering in this case. (The orthogonality scattering is important, however). For the HF molecule the single-configuration approximation is more severe, and leads to unphysical oscillations in the cross section in a narrow energy region above threshold. Nevertheless, the uncertainty remains within about 5%, and there are no difficulties in principle in extending our calculations to the multiconfigurational version. The potential scattering for HF is particularly important because of the strong dipolar interaction. Adding the quadrupole and polarization interactions leads to small but noticeable changes in the DA cross sections. Therefore the inclusion of the full electron-molecule interaction into the calculations of the continuum state might be important for dipolar and highly polarizable targets. In the present work we use a semiempirical potential for HF, but in future we plan to employ existing methods for *ab initio* calculations of the continuum state [29].

We should therefore note that the procedure implemented in the present work cannot be qualified as an *ab initio* study because it still contains some semiempirical adjustments: the choice of the neutral potential curve consistent with experimental data or other *ab initio* calculations, semiempirical adjustment of the negative-ion curve, and the semiempirical form of the potential for e -HF scattering. However, there is no difficulty in principle doing all calculations *ab initio* by employing the present method.

The good agreement of calculated enhancement in the threshold DA cross sections for HF with the experimental results of Allan and Wong [47] demonstrates the reliability of our method for a calculation of DA to molecules with relatively high, supercritical dipole moments. On the other hand, the calculated cross section decreases faster with energy than the experimental cross section of Abouaf and Teillet-Billy [46], which perhaps indicates the existence of another resonance at higher energies.

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APPENDIX A: INSTABILITIES IN INTEGRATION OF INHOMOGENEOUS EQUATIONS

For simplicity we consider a single differential equation of the type

$$u'' + \left[k^2 - \frac{l(l+1)}{r^2} - 2V(r) \right] u = br^{l+1}g(r), \quad (A1)$$

where $g(r)$ is a regular function (e.g., a Gaussian) that decays exponentially at $r \gg 1$. A general solution, regular at the origin, is

$$u(\rho) = \frac{u_1(\rho)}{k} \left[\int_0^\rho u_2(\rho')s(\rho')d\rho' + C \right] - \frac{u_2(\rho)}{k} \int_0^\rho u_1(\rho')s(\rho')d\rho', \quad (A2)$$

where C is an arbitrary constant, $\rho = kr$, $s(\rho) = b\rho^{l+1}g(\rho/k)/k^{l+3}$, and u_1 and u_2 are the regular and irregular solutions of the homogeneous equation defined by the following behavior near the origin:

$$u_1(\rho) \sim \frac{\rho^{l+1}}{(2l+1)!!}, \quad u_2(\rho) \sim \frac{(2l-1)!!}{\rho^l}. \quad (A3)$$

Consider now the first term in Eq. (A2) at $k \ll \rho \ll 1$ or $1 \ll r \ll 1/k$. Since $g(r)$ decays exponentially, we can extend the integration limit to ∞ and obtain

$$\begin{aligned} \int_0^\rho u_2(\rho')s(\rho')d\rho' &\approx \int_0^\infty \frac{(2l-1)!!}{(\rho')^l} \frac{b(\rho')^{l+1}}{k^{l+3}} g(\rho'/k) \\ &= \frac{b(2l-1)!!}{k^{l+1}} \int_0^\infty r g(r) dr. \end{aligned} \quad (A4)$$

Whereas the integral on the right-hand side is a regular number, the quantity $(2l-1)!!/k^{l+1}$ is enormously large for higher l and low enough k . This large contribution to u should be compensated for by the constant C for the physical solution. In principle this may be taken care of by matching the regular solution, obtained from the outward integration, with the solution with the required asymptotic behavior, obtained from the inward integration. However, due to the subtraction of two very large contributions, this procedure in practice leads to a significant loss of accuracy. Therefore direct numerical integration of Eq. (A1) is unstable.

APPENDIX B: SOME PROPERTIES OF SOLUTIONS OF HOMOGENEOUS DIFFERENTIAL EQUATIONS

Consider a homogeneous system of coupled differential equations similar to Eq. (32),

$$u'' + qu = 0, \quad (B1)$$

where q is a real symmetric matrix. Let u_1 and u_2 be any two solutions of Eq. (B1). Introduce the generalized Wronskian

$$W(u_1, u_2) = (u_1^T)' u_2 - (u_2^T)' u_1, \quad (B2)$$

and what we will call the adjoint Wronskian,

$$W^A(u_1, u_2) = u_1' u_2^T - u_2' u_1^T. \quad (B3)$$

Using Eq. (B1), we see immediately that $W' = 0$, i.e., W is independent of r , and can be calculated in the limit $r \rightarrow 0$ or $r \rightarrow \infty$. In all important cases W is just a constant times the unit matrix. In particular, if $u_1 = u^{(+)}$ and $u_2 = u^{(-)}$, from Eq. (33) we have $W = 2iI$. For two identical matrices $W = 0$, and we have an identity

$$(u_1^T)' u_1 = (u_1^T) u_1', \quad (\text{B4})$$

which means that $u_1' u_1^{-1}$ is a symmetric matrix for any solution u_1 . In particular, if u_1 is a regular solution, we obtain the symmetry of the R matrix.

Now multiply Eq. (B2) by $(u_1^T)^{-1}$ from the left and by $(u_2)^{-1}$ from the right. We obtain

$$(u_1^T)^{-1} (u_1^T)' - u_2' u_2^{-1} = W (u_1^T)^{-1} u_2^{-1}. \quad (\text{B5})$$

The matrices on the left are both symmetric, and therefore so is the right one:

$$u_2 u_1^T = u_1 u_2^T. \quad (\text{B6})$$

Using this property, we immediately obtain that the adjoint Wronskian $W^A(u_1, u_2)$ [Eq. (B3)], is also a constant times the unit matrix. Substituting $u_1 = u^{(+)}$, $u_2 = u^{(-)}$, we obtain Eq. (35).

Next consider

$$W^A(u^{(+)}, u^{(-)}) = (u^{(+)'})' (u^{(-)})^T - (u^{(-)'})' (u^{(+)})^T. \quad (\text{B7})$$

Using the relation

$$u^{(-)} = u^{(+)} - u^{(+)} S \quad (\text{B8})$$

and the symmetry of the S matrix, we obtain

$$W^A(u^{(+)}, u^{(-)}) = W^A(u^{(+)}, u^{(+)}). \quad (\text{B9})$$

Now calculating W^A at $r \rightarrow \infty$, we finally obtain

$$W^A(u^{(+)}, u^{(-)}) = 2iI, \quad (\text{B10})$$

which proves Eq. (36).

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