

## Dissociative attachment of electrons to vibrationally excited H<sub>2</sub>

A. Peet Hickman

*Molecular Physics Laboratory, SRI International, Menlo Park, California 94025*

(Received 9 April 1990; revised manuscript received 6 November 1990)

Calculations are reported of the dissociative attachment of low-energy (less than 5 eV) electrons to molecular hydrogen in the states  $v=0-9$  and  $J=0$ . The dynamics are treated using resonant scattering theory, fully including the nonlocal and energy-dependent shift and width operators. The necessary coupling terms are taken from the *ab initio* calculations of fixed- $R$  electron-H<sub>2</sub> scattering performed by Mündel, Berman, and Domcke [Phys. Rev. A **32**, 181 (1985)]. Good agreement with the available experimental data of Schulz and Asundi [Phys. Rev. **158**, 2 (1967)] and of Allan and Wong [Phys. Rev. Lett. **41**, 1791 (1978)] is achieved. Exploratory calculations were performed to investigate various local approximations to the nonlocal shift operator. The results suggest that the optimum local approximation will, in general, differ from the curve obtained in a fixed-nuclei structure calculation.

### I. INTRODUCTION

Dissociative attachment (DA) of electrons to molecular hydrogen is a process of great fundamental and practical interest. It is thought to be a primary source of the H<sup>-</sup> ions produced in hydrogen plasmas. The process may be schematically written



where  $v$  and  $J$  denote the vibrational and rotational quantum numbers of H<sub>2</sub>. Measurements for the absolute cross section for attachment to the ground state ( $v=J=0$ ) were reported by Schulz and Asundi,<sup>1</sup> and Allan and Wong<sup>2</sup> showed that the cross section increases dramatically as the internal energy of H<sub>2</sub> increases. They measured relative values of  $\sigma$  for  $v=0-4$  ( $J=0$ ), and found that the cross section increased roughly an order of magnitude for each increment of  $v$ .

This behavior was explained in 1978 by the analysis of Wadehra and Bardsley<sup>3</sup> based on the local complex potential model. They used *ab initio* potential curves available at that time, and fit a parametrized coupling function to the experimental data. The same coupling function was then used<sup>3-6</sup> to extend the calculations to other values of  $(v, J)$ , for which experimental data are not available.

Recent work in the calculation of potential curves and coupling terms for electron-molecule scattering has provided *ab initio* information of much greater reliability than was available ten years ago, and this information can be used to reexamine the treatment of dissociative attachment. For example, the recent calculations of Berman, Mündel, and Domcke<sup>7</sup> have provided the necessary matrix elements for a treatment of dissociative attachment of H<sub>2</sub> that fully includes the energy-dependent and nonlocal shift and width operators. These authors also report calculations<sup>8</sup> of DA of H<sub>2</sub> for  $v=0-2$  ( $J=0$ ), but the emphasis of their work was on vibrational excitation. We have found that their work, with some additional

analysis, provides a basis for much broader calculations of DA.

This paper is organized as follows. Section II presents the theory, including a summary of the resonant scattering theory and a discussion of specific coupling terms. Particular care is taken to handle the potentials and couplings in the range of internuclear separations  $R$  near  $3.0a_0$  where the  $^2\Sigma_u^+$  resonant state H<sub>2</sub><sup>-</sup> crosses the H<sub>2</sub> potential curve. Section III presents and discusses the numerical results, and Sec. IV contains concluding remarks.

### II. THEORY

#### A. Summary of resonant scattering theory

The formal theory of DA is well developed,<sup>8-11</sup> and we will present only the essential points to facilitate discussion of our implementation. The following summary follows the notation of Wadehra's review<sup>12</sup> to a large extent. We begin with the expression for the total wave function of the electron-molecule system:

$$\Psi(q, R) = \phi_d(q, R)F(R) + \sum_{\text{open}} \int d\varepsilon f_v(\varepsilon) \psi_\varepsilon(q, R) \chi_v(R). \quad (2)$$

$q$  refers collectively to the electron coordinates, and  $R$  is the internuclear separation. It is assumed that the fixed- $R$  electron-molecule wave functions have been determined:  $\phi_d$  is a discrete state, corresponding to H<sub>2</sub><sup>-</sup>, and  $\psi_\varepsilon$  is an electron-molecule-scattering wave function. The vibrational wave functions of H<sub>2</sub> are  $\chi_v$ . The treatment of DA requires the determination of  $F(R)$ , the wave function describing the nuclear motion. By substituting Eq. (2) into Schrödinger's equation and formally solving for the expansion coefficients  $f_v(R)$ , one can derive the following equation for  $F(R)$ :

$$\left[ \frac{\hbar^2}{2M} \frac{d^2}{dR^2} - V_d(R) + E \right] F(R) = V(R, E - E_{v_0}) \chi_{v_0}(R) + \left[ \bar{\Delta} - \frac{i}{2} \bar{\Gamma} \right] F(R). \quad (3)$$

The total energy  $E$  is the sum of the asymptotic ( $R \rightarrow \infty$ ) kinetic energy of the electron and the vibrational energy of the molecule, which is  $E_v$  for vibrational state  $v$ . The initial vibrational state of  $\text{H}_2$  is  $v_0$ .  $V_d(R)$  is defined as a matrix element of the electronic Hamiltonian  $H_{el}$

$$V_d(R) = \langle \phi_d | H_{el} | \phi_d \rangle. \quad (4)$$

$\bar{\Delta}$  and  $\bar{\Gamma}$  are nonlocal, energy-dependent operators whose action on the function  $F(R)$  yields a function of  $R$  defined as follows:

$$\left[ \bar{\Delta} - \frac{i}{2} \bar{\Gamma} \right] F = \int dR' \sum_{\text{open } v} \chi_v(R) \chi_v(R') \times \left[ \Delta(R, R', E - E_v) - \frac{i}{2} \Gamma(R, R', E - E_v) \right] \times F(R'), \quad (5)$$

where

$$\Delta(R, R', \varepsilon) = \text{P} \int d\varepsilon' \frac{V(R, \varepsilon') V(R', \varepsilon')}{\varepsilon - \varepsilon'}, \quad (6)$$

$$\Gamma(R, R', \varepsilon) = 2\pi V(R, \varepsilon) V(R', \varepsilon), \quad (7)$$

$$V(R, E) = \langle \phi_d | H_{el} | \psi_\varepsilon \rangle. \quad (8)$$

Equation (3) is solved for the boundary conditions that  $F(R) = 0$  for  $R = 0$ , and  $F(R)$  is an outgoing wave asymptotically. The cross section for DA is then

$$\sigma_{\text{DA}} = \frac{\pi^2 \hbar k}{\varepsilon M} \lim_{R \rightarrow \infty} |F(R)|^2. \quad (9)$$

This formulation can be related to the parameters describing the fixed- $R$  resonant scattering. At each  $R$ , the electron-scattering cross section from the molecule exhibits a resonance of width  $\Gamma(R)$  at an electron kinetic energy  $E_{\text{res}}(R)$ . It is convenient to define a potential curve  $V_{\text{res}}(R)$  that combines the electron-scattering energy with the energy of the bound-state  $\text{H}_2$  target:

$$V_{\text{res}}(R) = V_{\text{H}_2}(R) + E_{\text{res}}(R), \quad (10)$$

where  $V_{\text{H}_2}(R)$  is the ground-state  $\text{H}_2$  potential.  $V_{\text{res}}(R)$  is shifted by an amount  $\Delta(R)$  from the zeroth-order discrete state energy  $V_d(R)$ .  $V_{\text{res}}(R)$ ,  $E_{\text{res}}(R)$ , and  $\Gamma(R)$  are related as follows:

$$V_{\text{res}}(R) = V_d(R) + \Delta(R), \quad (11)$$

where

$$\Delta(R) = \Delta(R, R, E_{\text{res}}(R)). \quad (12)$$

The width ( $\Gamma$ ) of the resonance at fixed  $R$  is given by

$$\Gamma(R) = 2\pi V(R, E_{\text{res}}(R))^2. \quad (13)$$

The distinction between  $V_{\text{res}}(R)$  and  $V_d(R)$  has not always been maintained. It is often assumed that the operator  $\Delta$  on the right-hand side (rhs) of Eq. (3) can be neglected, and that  $V_d(R)$  on the left-hand side (lhs) can be replaced by  $V_{\text{res}}(R)$ . This simplification corresponds to approximating the dynamical operator  $\bar{\Delta}$  by  $\Delta(R)$  in Eq. (3), and then assuming the closure relation for the sum over open vibrational states. In the present work, we utilize recent calculations<sup>7,8</sup> for  $V(R, \varepsilon)$ , which allows us explicitly to include the nonlocal shift operator.

## B. Electronic matrix elements

Calculations are available in the literature for nearly all the necessary coupling terms for DA of  $\text{H}_2$ . Excellent potential curves for  $\text{H}_2$  have been obtained;<sup>13</sup> these were used to calculate the vibrational wave functions  $\chi_v$ .  $E_{\text{res}}(R)$  has been calculated by Berman, Mündel, and Domcke.<sup>7</sup> These authors showed that  $E_{\text{res}}(R)$  could be unambiguously defined as the electron-scattering energy at which the eigenphase sum equals  $\pi/2$ .

For the essential matrix element  $V(R, \varepsilon)$ , we have fit the numerical values calculated by Mündel and co-workers<sup>7,8</sup> by a convenient analytic function. Although Mündel, Berman, and Domcke<sup>8</sup> reported a nine-parameter analytic fit to their calculations, we have found it preferable to repeat the fit using a different analytic form. Some difficulty was encountered in trying to use the functional form reported in Ref. 8.  $V(R, \varepsilon)$  approaches a nonzero constant asymptotically (as  $R \rightarrow \infty$ ). Also, Table I in Ref. 8 contains typographical errors.

A good fit to the calculated points was obtained with the following analytic function:

$$V(R, \varepsilon) = \frac{A(R) \varepsilon^{3/4}}{(\varepsilon + B)^2}. \quad (14)$$

This formula is physically plausible. If we consider the matrix element between a bound hydrogenic function and an energy-normalized  $p$ -wave scattering function  $(2k/\pi)^{1/2} j_1(kr)$ , the result is<sup>14</sup>

$$(2k/\pi)^{1/2} \int_0^\infty e^{-r/r_0} j_1(kr) r^2 dr \propto \frac{k^{3/2}}{(k^2 + r_0^{-2})^2}. \quad (15)$$

Since  $\varepsilon = \frac{1}{2} k^2$ , Eq. (15) is consistent with Eq. (14) and yields the correct threshold behavior.

The most accurate fit could be achieved by letting both  $A$  and  $B$  be functions of  $R$  in Eq. (14). However, considerable simplification of the calculations results if  $B$  is a constant. This point will be discussed below. Fortunately, we found that a reasonably accurate fit could still be obtained if  $B$  is a constant. Figure 1 shows the results of a least-squares fit to the calculations of Berman, Mündel, and Domcke,<sup>7</sup> using the analytic form of Eq. (14). The constant  $B = 7.15$  eV was obtained in the fit. This approach also provides a natural way to extrapolate  $V(R, \varepsilon)$  to large values of  $R$ : one keeps the same  $B$  and adopts a sensible asymptotic form for  $A(R)$ . As shown in Fig. 2,

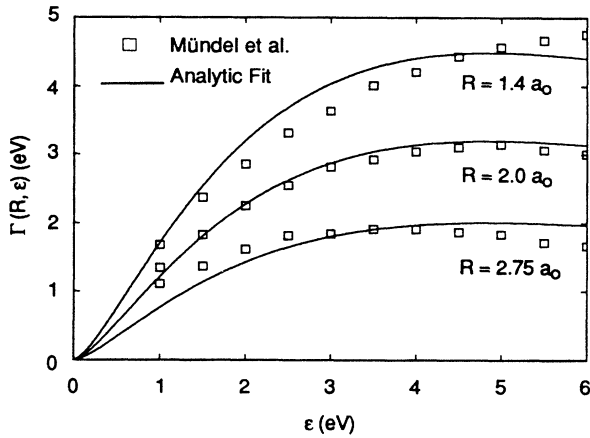


FIG. 1. Comparison of the numerical values  $\Gamma(R, \epsilon) = 2\pi|V(R, \epsilon)|^2$  calculated by Mündel and co-workers with the analytic fit used in the present work.

the values of  $A(R)$  fit in the range  $1.4a_0 < R < 2.75a_0$  (for which calculations were reported) suggest a linear extrapolation out to the  $R$  for which  $A(R)$  is zero.

The advantage of the form Eq. (14) for  $V(R, \epsilon)$  is twofold. First, the principal part integral in the definition of the shift operator [Eq. (6)] can be done analytically. Second, a separable form of the shift operator results, permitting Eq. (3) to be solved by Bardsley's Green's-function method.<sup>15,16</sup> We consider the principal part integral in this section, and defer discussion of the method of solution to Sec. II C.

We now consider

$$\Delta(R, R', \epsilon) = P \int_0^\infty \frac{A(R)A(R')(\epsilon)^{3/2}d\epsilon'}{(\epsilon' + B)^4(\epsilon - \epsilon')}, \quad (16)$$

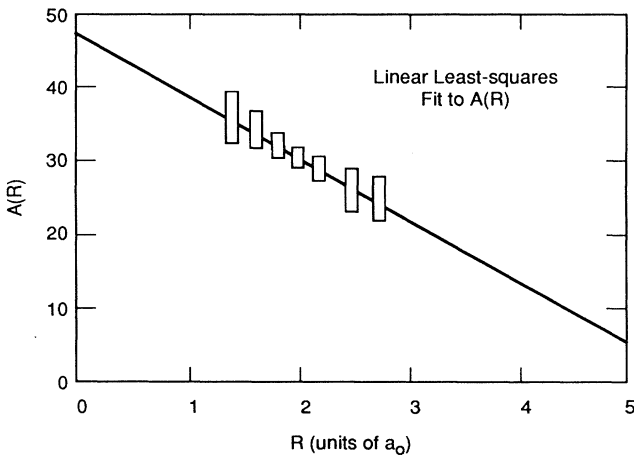


FIG. 2. Determination of the least-squares fit to  $A(R)$ . The values of  $\Gamma(R, \epsilon) = 2\pi|V(R, \epsilon)|^2$  shown in Fig. 1 and calculated in Ref. 8 can be inverted using Eq. (14) to give a value of  $A(R)$  for each  $(R, \epsilon)$  pair. The range of values of  $A$  thereby calculated at each  $R$  is indicated by the boxes.

where  $P$  denotes the principal part integral. Simplification follows by the change of variable to  $x = \epsilon'/B$  and by the introduction of a factor of  $\pi/16$  for future convenience:

$$\Delta(R, R', \epsilon) = -\frac{\pi}{16} A(R)A(R')B^{5/2}p(\epsilon/B), \quad (17)$$

where

$$p(a) = \frac{16}{\pi} P \int_0^\infty \frac{x^{3/2}dx}{(x+1)^4(x-a)}. \quad (18)$$

The function  $p(a)$  only needs to be evaluated in the interval  $[-1, 1]$ . The value of  $p$  elsewhere follows from the symmetry relation

$$p(1/a) = -ap(a), \quad (19)$$

which is easily verified by writing the integral expression Eq. (18) for  $p(1/a)$ , and then changing variables to  $y = 1/x$ .

Figure 3 illustrates the values of  $p(a)$  calculated numerically. The special values  $p(0) = 1$ ,  $p(1) = 0$ , and  $dp/da(0) = 5$  follow from Eqs. (18) and (19).

We now illustrate the explicit values of the coupling matrix elements used. Particular attention is paid to the region of  $R$  near  $3a_0$ . For  $R > 3a_0$ , there exists a well-defined bound-state  $H_2^-$  at an energy below the corresponding  $H_2$  energy. For fixed  $R < 3a_0$ , there exists a scattering resonance at an energy  $E_{\text{res}}(R) > 0$ . Formally, one expects<sup>17</sup> the bound state at large  $R$  to join smoothly with the resonance at small  $R$ ; the potential curves adopted to treat DA must behave this way as well. Using the values of  $E_{\text{res}}(R)$  calculated by Berman, Mündel, and Domcke<sup>7</sup> for  $R < 3a_0$ , and the potential curve calculated by Senekowitsch *et al.*<sup>18</sup> for  $R > 3a_0$ , we found indeed that the  $H_2^-$  curve at large  $R$  could be smoothly joined with the curve  $V_{\text{res}}(R)$  defined by Eq. (10). Another way of stating this is that for  $R > 3a_0$ ,  $E_{\text{res}}(R)$  is negative and corresponds to a bound state.

We can now define the potential curve  $V_d(R)$  for all values of  $R$ . Since  $E_{\text{res}}(R)$  has been shown to be a smooth

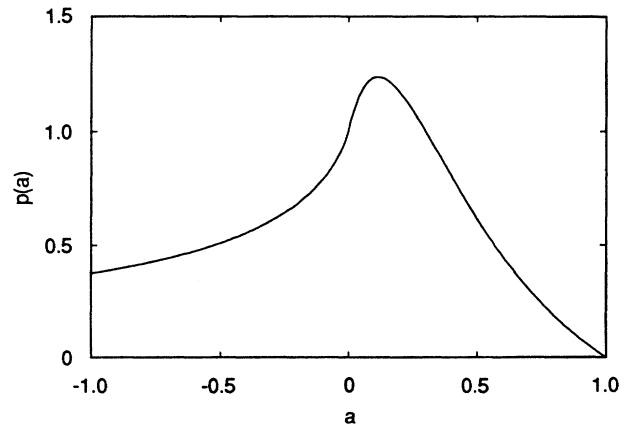


FIG. 3. Reduced function used to determine the principal part integral defined by Eq. (18).

and well-behaved function of  $R$  near  $R = 3a_0$ , there is no difficulty in using the definition of the shift [Eqs. (11), (12), and (17)] to determine  $V_d(R)$  for both positive and negative values of  $E_{\text{res}}(R)$ :

$$V_d(R) = V_{\text{H}_2}(R) + E_{\text{res}}(R) - \Delta(R). \quad (20)$$

The potential curves determined are shown in Fig. 4.

$$\left[ \frac{\hbar^2}{2M} \frac{d^2}{dR^2} - V_d(R) + E \right] F(R) = V(R, E - E_{v_0}) \chi_{v_0}(R) + \int dR' \sum_{\substack{v \\ \text{open}}} \chi_v(R) \chi_v(R') A(R) A(R') [g_\Delta(E - E_v) - i\pi g_\Gamma(E - E_v)] F(R'), \quad (21)$$

where

$$g_\Gamma(\varepsilon) = \frac{\varepsilon^{3/2}}{(\varepsilon + B)^4} \quad (22)$$

and

$$g_\Delta(\varepsilon) = -\frac{\pi}{16} B^{-5/2} p(\varepsilon/B). \quad (23)$$

Bardsley's Green's-function method<sup>15,16</sup> can be used to reduce the problem to a set of linear equations whose coefficients involve the matrix elements of the Green's function for the lhs of Eq. (20). This function is defined as

$$G(R', R) = C^{-1} F_1(R_<) F_2(R_>), \quad (24)$$

where  $F_1(R)$  is the regular solution of Eq. (21) with the rhs set to zero which satisfies the boundary conditions  $F_1(0) = 0$  and  $F_1(R) \rightarrow \sin(kR + \delta)$  as  $R \rightarrow \infty$ . The irregular solution  $F_2(R)$  satisfies  $F_2(R) \rightarrow \exp[i(kr + \delta)]$  as  $R \rightarrow \infty$ . For this choice of asymptotic normalization, the Wronskian  $C = -k/2M$ . The matrix elements  $G_{vv'}$  are

### C. Working equations

We now describe the solution of Eq. (3). The analysis of Sec. II B has led to explicit forms of the shift and width operators that can be handled with standard methods. The crucial point is that the  $R$  and  $R'$  dependence of  $\Delta$  and  $\Gamma$  is identical. One can rewrite Eq. (3) as

defined by

$$G_{vv'} = \int_0^\infty dR \int_0^\infty dR' A(R) \chi_v(R) G(R, R') A(R') \chi_{v'}(R'). \quad (25)$$

One then solves the set of linear equations  $\underline{A} \underline{x} = \underline{b}$ , where

$$x_v = \int_0^\infty \chi_v(R) A(R) F(R) dR, \quad (26)$$

$$b_v = g_\Gamma(E - E_{v_0}) G_{vv_0}, \quad (27)$$

and

$$A_{vv'} = \delta_{vv'} - [g_\Delta(E - E_{v'}) - i\pi g_\Gamma(E - E_{v'})^2] G_{vv'}. \quad (28)$$

The asymptotic form of  $F(R)$  can be determined from the  $x_v$  just as in previous work,<sup>16-19</sup> and from that the cross sections can be evaluated.

## III. RESULTS AND DISCUSSION

### A. Calculations of cross sections and rates

Cross sections for DA of  $\text{H}_2$  through the  $^2\Sigma_u^+ \text{H}_2^-$  state have been calculated for  $J=0$  and  $v=0-9$ , and for electrons from threshold up to 4–5 eV. Results for the cross sections as a function of incident electron energy are shown in Fig. 5. These calculations include the full energy-dependent and complex shift and width operators. The cross sections exhibit oscillatory structure near threshold, which may be related to the energy dependence of the width operator. We found that the oscillations persisted when the nonlocal shift was replaced by a local shift. However, the structure was not present in earlier calculations we performed with a nonlocal but energy-dependent width, nor was it seen in the calculations of Wadehra and Bardsley,<sup>3</sup> who used a local shift and a local width. This comparison suggests that the energy-dependent factors in the sum over vibrational states in Eq. (21) may be the origin of the structure. These terms spoil the closure approximation, in which the sum is replaced by a Dirac  $\delta$  function, and which underlies the reduction to the local complex potential model.

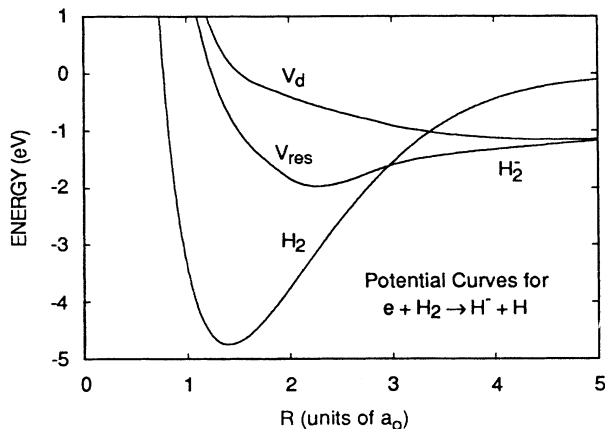


FIG. 4. Relevant potential curves for the dissociative attachment of electrons to  $\text{H}_2$ .

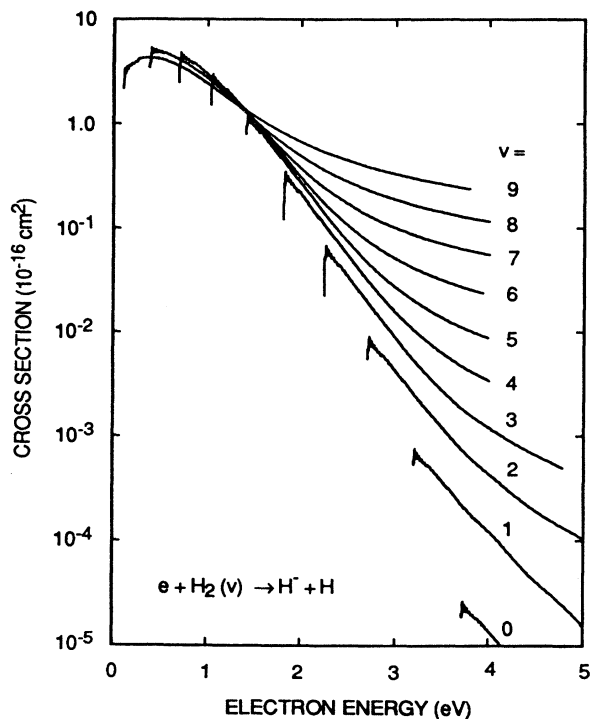


FIG. 5. Calculated cross section for dissociative attachment of electrons with  $\text{H}_2^+$  ( $v, J=0$ ) through the  $^2\Sigma_u$  resonant state. The full energy-dependent and nonlocal shift and width operators were used for these calculations.

The calculations can be compared with experimental data, and with other calculations in the literature, in several different ways. Figure 6 shows the cross section for attachment by  $\text{H}_2$  ( $v=0$ ) as a function of energy. Several recent calculations are compared with the data of Schulz and Asundi.<sup>1</sup> The calculated peak values are very similar. It is plausible that the calculations are all larger

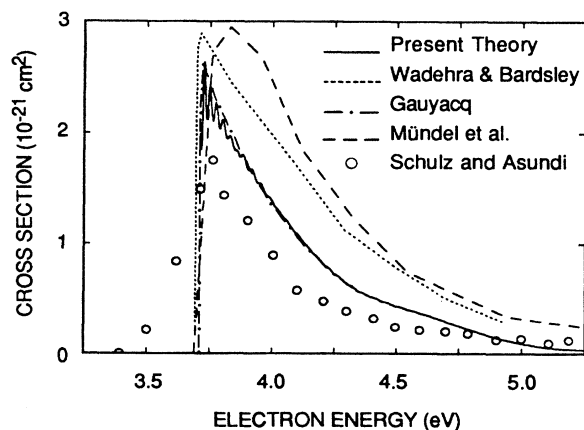


FIG. 6. Calculated cross section for dissociative attachment of electrons with  $\text{H}_2$  ( $v=0, J=0$ ) is compared with several previous calculations and with the experimental data of Schulz and Asundi.

than the experiment; Gauyacq<sup>20</sup> has pointed out that convoluting his calculation with an electron-energy distribution whose full width at half maximum (FWHM) is 300 meV would decrease the calculations from 2.3 to  $1.5 \times 10^{-5} \text{ \AA}^2$ . The primary difference between the calculations is the width of the threshold peak. The present calculation agrees closely with that of Gauyacq,<sup>20</sup> and obtains a FWHM of about 340 meV; the calculated widths of Wadehra and Bardsley<sup>3</sup> and Mündel, Berman, and Domcke<sup>8</sup> are about 500 and 530 meV, respectively. Schulz and Asundi<sup>1</sup> reported two sets of data taken under different conditions. The set with the narrower width, about 400 meV, is shown; the width of the other set was about 600 meV. Further experimental data would be desirable to differentiate between the various calculations.

Allan and Wong<sup>2</sup> have measured the relative cross sections at threshold for  $v=0-4$ , and we compare our calculations with their data in Fig. 7. The relative experimental measurements have been converted to absolute cross sections by using the measurements of Schulz and Asundi for  $v=0$  ( $=1.6 \times 10^{-5} \text{ \AA}^2$ ). Comparison with other calculations is also possible over the range  $v=0-9$ . We note that Wadehra and Bardsley<sup>3,4</sup> and Wadehra<sup>5,6</sup> fit their calculations to the experimental data, and used the same coupling potentials and matrix elements for the calculations at higher  $v$ . The present calculations are closest to those of Mündel, Berman, and Domcke<sup>8</sup> for  $v=0-2$ , who also took into account the nonlocal, energy-dependent shift and width operators. The present calculation rests on a fully numerical solution of the nuclear wave equation [Eq. (21)], which was facilitated by a particular choice of the form of the electronic coupling matrix element [Eq. (14)]. Mündel, Berman, and Domcke fit  $V_d(R)$  with a Morse potential, and treated the shift and width operators by an expansion in a Lanczos basis. We believe that the present approach uses more accurate potentials for the range of internuclear distance where the

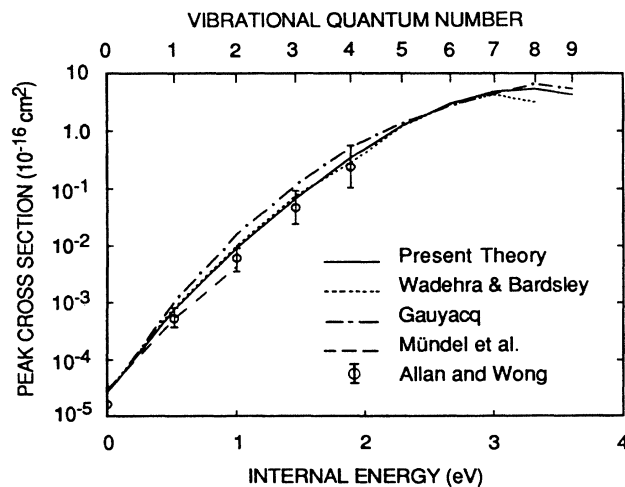


FIG. 7. Peak cross section for dissociative attachment as a function of the internal energy of the molecule. The scale on the top of the figure shows the corresponding vibrational quantum number for  $J=0$ .

$H_2$  potential crosses the  $H_2^-$  curve. This range is crucial to DA, but less important to vibrational excitation, which was the emphasis of the work of Mündel, Berman, and Domcke.<sup>8</sup> Finally, we note that the present calculations agree well with those of Gauyacq,<sup>20</sup> which were based on the zero-range-potential formalism.

Extensive calculations were carried out by Wadehra and Bardsley<sup>3,4</sup> and Wadehra<sup>5,6</sup> using the local complex potential model; many of the results were presented as rate constants depending on an average energy  $\bar{E} = \frac{3}{2}kT$ . We adopt the same nomenclature for easy comparison with their results. Figure 8 shows rather close agreement between the present calculations and the previous calculations based on the local complex potential model. Although the logarithmic scale minimizes the quantitative differences, all general trends are in essential agreement.

Finally, the dynamical calculations of DA depend on the potentials and matrix elements in the range of  $R > 3a_0$ , where  $H_2^-$  is a true bound state. A series of calculations was performed in which  $A(R)$  was arbitrarily set to zero for  $R > 3a_0$ , thereby eliminating any contribution from this range of  $R$ . The total cross sections for DA decreased about 20–30%. Since Mündel and co-workers<sup>7,8</sup> only reported numerical values for  $V(R, \epsilon)$  in the range  $R = 1.4$ – $2.75a_0$ , the  $A(R)$  we used for larger  $R$  is an extrapolation. This test provides a measure for the uncertainty in our calculations due to our extrapolation of  $A(R)$ .

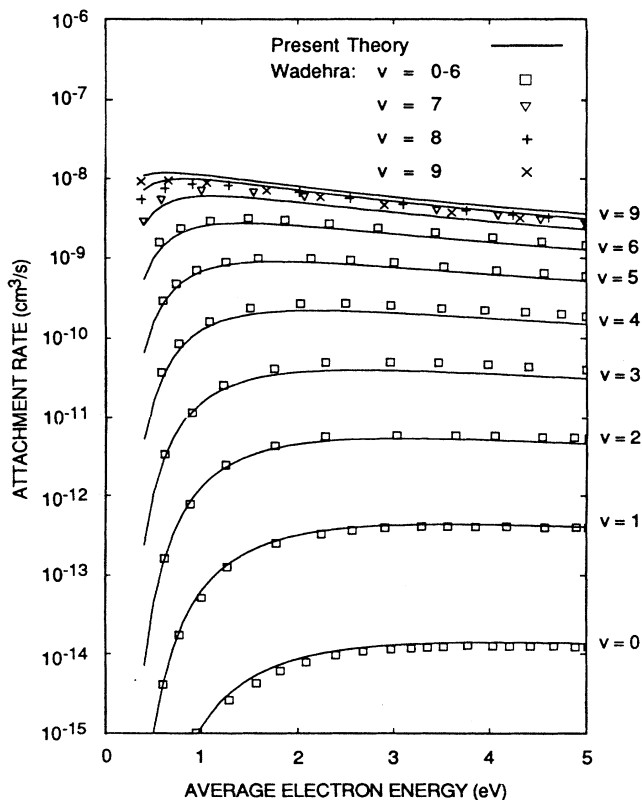


FIG. 8. Comparison of rate constants for dissociative attachment with the corresponding calculations of Wadehra based on the local complex potential model.

### B. Accuracy of the local complex potential model

The most surprising aspect of the present results is that the calculations based on the local complex potential (LCP) appear to be fairly satisfactory, at least when one looks at an average quantity like the rate constant. Is there a physical basis for replacing the nonlocal operators  $\tilde{\Delta} - (i/2)\tilde{\Gamma}$  with a simpler, local form? Mündel, Berman, and Domcke<sup>8</sup> performed a comparison for  $v=0$  and concluded that the LCP was a “stunning failure.” They noted that the results of the LCP could be as much as a factor of 10 large. The explicit expressions we have used for the width and particularly the shift operator provide a tool for monitoring the accuracy of the final calculation as successive approximations are invoked to simplify the shift or width. Our results confirm the need to consider the full operators, but suggest situations where an optimum local shift can be defined.

We begin our analysis with the explicit expression for the action of the shift operator on the nuclear wave function, which follows from Eqs. (21) and (23),

$$\begin{aligned} \tilde{\Delta}F &= \frac{\pi}{16} B^{-5/2} A(R) \\ &\times \int dR' \sum_{\substack{v \\ \text{open}}} \chi_v(R) \chi_v(R') \\ &\times p \left[ \frac{E - E_v}{B} \right] A(R') F(R'). \end{aligned} \quad (29)$$

The operator  $\tilde{\Delta}$  is both nonlocal, because of the integrals over  $R'$ , and energy dependent, because of the terms involving  $(E - E_v)$ . We note that the constant  $B$  was determined to be 7.15 eV, and that for electrons at threshold for DA,  $E - E_v$  ranges from 3.7 eV ( $v=0$ ) to 0.14 eV ( $v=9$ ). Hence, for our calculations  $(E - E_v)/B < 0.5$ . From Fig. 3 it appears that the energy variation of  $p[(E - E_v)/B]$  in this range is not large and that  $p(0) = 1$  could be substituted into Eq. (29) as an approximation. If this is done, the shift operator is reduced to an energy-independent but still nonlocal operator. The arguments for further simplification are well known; one assumes that the sum over open channels in Eq. (29) is close to the sum over all channels (including the continuum), which satisfies the completeness relation

$$\sum_v \chi_v(R) \chi_v(R') = \delta(R - R'). \quad (30)$$

Again specializing to  $H_2$ , we note that the sum always includes at least ten terms, since the asymptotic energy of  $H + H^-$  is greater than the vibrational energy of  $H_2$  for  $v=0$ – $9$ . If we assume that the sum is complete, the shift operator is reduced to the following local operator:

$$\Delta F = - \frac{\pi}{16} B^{-5/2} A(R)^2 F(R). \quad (31)$$

This form provides a simple analytic form for the shift. The determination of an explicit analytic form for the coupling matrix element  $V(R, \epsilon)$  has led to an approximate form of a local shift that is different from the normal local approximation to the shift. It is usually argued

that the local shift is the static shift that is obtained when one solves the fixed nuclei scattering problem [Eq. (11)]. We have tested these two forms of the local shift.

A similar argument can be used to reduce the nonlocal width operator to a local form. In this case, however, there is no clear way to eliminate the energy dependence as there was for the shift. Substituting  $E_{\text{res}}(R)$  for  $E - E_v$  in the expression for  $\Gamma(R, R, E - E_v)$  in Eq. (5) is the most straightforward approach. As expected,<sup>12,21</sup> test calculations with such an energy-independent but nonlocal width show spurious threshold behavior: the cross section decreases discontinuously (generally less than 10%) as a new channel for vibrational excitation opens up. The calculations also suggested that the sum over open vibrational states was converged within 10–20%.

We performed a series of calculations to test the various approximations to the shift operator. In all cases the nonlocal and energy-dependent width was preserved. We found that the local shift defined by Eq. (31) was a reasonably good approximation. Figure 9 compares the results with the local shift and with the full shift operator. The largest error, about a factor of 2, occurs for  $v=0$ , and the approximation rapidly converges for increasing  $v$ . This behavior is completely consistent with the arguments that led to the local approximation in the first place.  $(E - E_v)/B$  at threshold is largest for  $v=0$ , and becomes progressively smaller for larger  $v$ . Hence approximating  $p[(E - E_v)/B]$  by  $p(0)$  should become

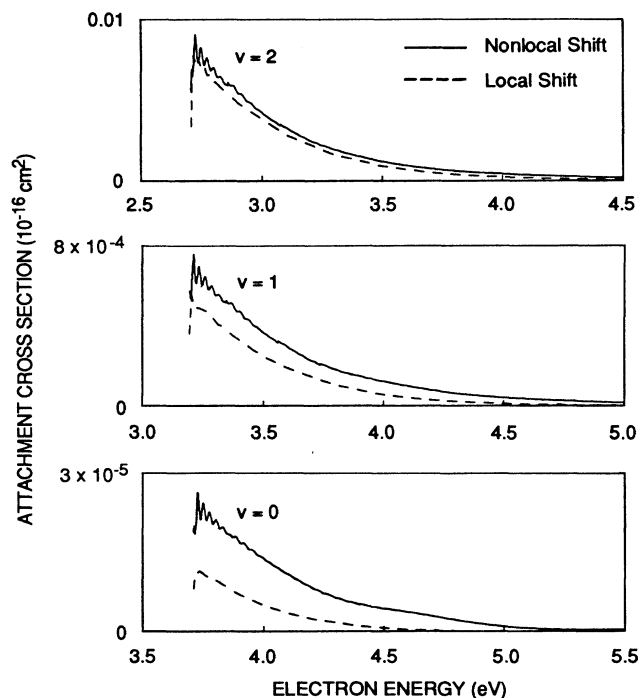


FIG. 9. Comparison of the cross section for dissociative attachment calculated using the full energy-dependent, nonlocal shift operator with a calculation using the local shift defined by Eq. (31). The energy-dependent, nonlocal width operator was used for both calculations.

progressively more accurate for larger initial  $v$ , and this behavior is exhibited by Fig. 9.

We also performed calculations in which the local shift was approximated by the fixed- $R$  shift defined by Eq. (11). As before, the energy-dependent and nonlocal width operator was used. For  $v=0$  the cross sections were about an order of magnitude too large, confirming the observation of Mündel, Berman, and Domcke<sup>8</sup> that this form of the local shift is a poor approximation. The cross sections were generally less accurate than those obtained with Eq. (31), although the results were within a few percent for  $v=5-9$ .

The two local potentials corresponding to the alternative local shifts are compared in Fig. 10.  $V_{\text{local}}$  is obtained by adding the local shift defined by Eq. (31) to  $V_d$ ; it led to reasonably accurate cross sections.  $V_{\text{res}}$  was defined earlier in Eqs. (11) and (12) as the position of the fixed-nuclei electron-scattering resonance. It is the curve that would be obtained in a standard fixed-nuclei calculation and we have seen that it does not lead to accurate cross sections.

These results demonstrate that part of the failure of the LCP reported in Ref. 8 can be attributed specifically to the choice of a local shift, and that the LCP can be improved by alternative choices of  $\Delta(R)$ . However, the optimum choice in the present case is not the fixed-nuclei form one might expect on physical grounds. These results provide a rationale for the success of Wadehra and Bardsley's calculations<sup>3-6</sup> based on the LCP model. Because of the accuracy of a local shift constructed by well-defined mathematical approximations, it appears plausible that a fitting procedure would lead to a legitimate, approximate local shift and width. However, using *ab initio* fixed-nuclei shifts and widths in a LCP model calculation can lead to serious errors.

#### IV. CONCLUDING REMARKS

Calculations have been reported of the dissociative attachment of low-energy electrons to molecular hydrogen

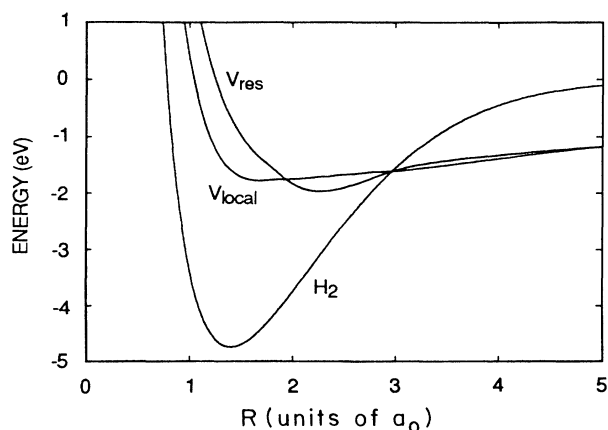


FIG. 10. Comparison of two forms of the local potential used for the results presented in Fig. 9. The local potentials  $V_{\text{res}}$  and  $V_{\text{local}}$  are obtained by adding to the potential  $V_d$  different local approximations for the shift operator.

in several vibrational levels. The calculations are based on fully *ab initio* calculations, obtained from the literature, of the potential curves and electronic-structure matrix elements that characterize the fixed- $R$  electron- $H_2$  scattering. The present calculations have fully included the energy-dependent and nonlocal width and shift operators.

By monitoring the accuracy of the calculations as the shift and width operators are reduced to local form, we have demonstrated that a poor choice of the local shift can seriously degrade the accuracy of the results, even if the correct, energy-dependent and nonlocal width is used. Unfortunately, the best choice of a local resonance potential curve, which follows from the optimum local shift, is not the one available from fixed-nuclei calculations of the resonant potential curve. Furthermore, our results suggest that a satisfactory local approximation to the shift operator may not always exist. Our experience with  $H_2$  suggests that an important requirement is that several vibrational channels be open at the threshold for DA. For

$H_2$ , ten vibrational channels are available at this energy, so the requirement is satisfied. The situation could be quite different for other systems.

This analysis of the results underscores the need for detailed electronic-structure calculations of the fixed- $R$  electron- $H_2$  scattering. In particular, the energy-dependent matrix element  $V(R, \epsilon)$  coupling the resonant state with the continuum must be obtained for a definitive calculation. The present work has shown that once the necessary fixed-nuclei information has been determined, the dynamics equations involving energy-dependent and nonlocal operators can be efficiently formulated and solved.

#### ACKNOWLEDGMENTS

The author acknowledges helpful conversations with W. Domcke, T. O'Malley, and J. Wadehra. This research was supported by the U.S. Air Force Office of Scientific Research under Contract No. F49620-88-K-0005.

---

<sup>1</sup>G. J. Schulz and R. K. Asundi, *Phys. Rev.* **158**, 2 (1967).

<sup>2</sup>M. Allan and S. F. Wong, *Phys. Rev. Lett.* **41**, 1791 (1978).

<sup>3</sup>J. M. Wadehra and J. N. Bardsley, *Phys. Rev. Lett.* **41**, 1795 (1978).

<sup>4</sup>J. M. Wadehra and J. N. Bardsley, *Phys. Rev. A* **20**, 1398 (1979).

<sup>5</sup>J. M. Wadehra, *Appl. Phys. Lett.* **35**, 917 (1979).

<sup>6</sup>J. M. Wadehra, *Phys. Rev. A* **29**, 106 (1984).

<sup>7</sup>M. Berman, C. Mündel, and W. Domcke, *Phys. Rev. A* **31**, 641 (1985).

<sup>8</sup>C. Mündel, M. Berman, and W. Domcke, *Phys. Rev. A* **32**, 181 (1985).

<sup>9</sup>T. F. O'Malley, *Phys. Rev. A* **150**, 14 (1966).

<sup>10</sup>J. N. Bardsley, *J. Phys. B* **1**, 365 (1968).

<sup>11</sup>W. Domcke, C. Mündel, and L. S. Cederbaum, *Comments At. Mol. Phys.* **20**, 293 (1987).

<sup>12</sup>J. M. Wadehra, in *Nonequilibrium Vibrational Kinetics*, edited by M. Capitelli (Springer-Verlag, Berlin, 1986).

<sup>13</sup>W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

<sup>14</sup>I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980).

<sup>15</sup>J. N. Bardsley, *J. Phys. B* **1**, 349 (1968).

<sup>16</sup>A. Giusti-Suzor, J. N. Bardsley, and C. Derkits, *Phys. Rev. A* **28**, 682 (1983).

<sup>17</sup>W. Domcke, *J. Phys. B* **14**, 4889 (1981).

<sup>18</sup>J. Senekowitsch, P. Rosmus, W. Domcke, and H.-J. Werner, *Chem. Phys. Lett.* **111**, 211 (1984).

<sup>19</sup>A. P. Hickman, *J. Phys. B* **20**, 2091 (1987).

<sup>20</sup>J. P. Gauyacq, *J. Phys. B* **18**, 1859 (1985).

<sup>21</sup>J. P. Gauyacq, *Dynamics of Negative Ions* (World Scientific, Singapore, 1987), pp. 160 and 161.