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# Nonlocal effects in dissociative electron attachment to H_2

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Electron scattering by diatomic molecules involving the formation of a single resonance is treated within the configuration-interaction formalism. A technique is presented for solving the resulting nonlocal integro-differential equation for the nuclear motion in the resonant state. This technique is applied to the scattering of electrons by molecular hydrogen (and its isotopes) via the formation of $X\,^2\Sigma_u^+$ resonance, using a semiempirical model for the resonant state. Numerical cross sections for dissociative attachment, to H_2, of electrons with energies below 5 eV are presented and compared both with available experimental data and with those obtained using the local approximation for the complete integro-differential equation. In contrast to the local theory, the nonlocal theory predicts cross sections that exhibit discontinuities at energies at which a new vibrational channel opens up. We also give an upper bound for attachment cross sections that holds for all isotopes of molecular hydrogen for all values of the incident electron energies.

I. INTRODUCTION

The process of dissociative electron attachment to molecular hydrogen,

$$e^- + H_2 \rightarrow H + H^- \ ,$$
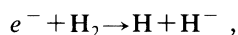
is currently of considerable practical interest as a possible source of production of negative hydrogen ions to be used for generation of neutral particle beams. For dissociative attachment to occur, the incoming electron and neutral target molecule form an intermediate resonant anion state, which can decay by autodetaching the electron. The motion of the nuclei in this resonant state is governed by a wave function $\xi(\mathbf{R})$, which satisfies an integro-differential equation involving a complex, nonlocal potential. In our previous calculations[1] we solved this equation by making use of a local approximation to the nonlocal integro-differential equation. As a part of this local approximation, one assumes that the set of vibrational levels which are accessible for a given incident electron energy can be regarded as complete. While this approximation may yield acceptable values for the cross sections well above threshold, it is expected to be less accurate near threshold where there are fewer energetically open vibrational channels. Results published previously by other investigators,[2] by using a nonlocal complex theory, have indicated that the local results for attachment cross sections could differ from the nonlocal results by nearly an order of magnitude. It is therefore of interest to solve the full nonlocal integro-differential equation for the nuclear wave function $\xi(\mathbf{R})$ near threshold and to compare the resulting nonlocal attachment cross sections with those that utilize the nuclear wave function $\xi(\mathbf{R})$, which is obtained using the local approximation to the full integro-differential equation. Besides providing an assessment of the effect of the local approximation on the electron attachment cross sections, the present calculations will also provide cross sections for H^- production which are more accurate than previously calculated.[1]

In the present paper we shall first outline the underlying theory and present the nonlocal equation for the nuclear wave function; next, we shall discuss our numerical technique for solving this equation and the potentials used in the present computations; finally, we will compare our present nonlocal cross sections both to those obtained earlier using the local version of the theory and to the corresponding experimental values.

II. NONLOCAL EQUATION FOR RESONANT SCATTERING

The theory of resonant scattering adopted by us was first developed by Fano[3] and applied to the scattering of electrons by diatomic molecules in the work of O'Malley[4] and Bardsley.[5] Although the basic approach employed in the present paper has been widely used, some authors[2] use slightly different assumptions and definitions in the derivation of the nonlocal equation that governs the motion of the nuclei in the resonant state. For clarity, then, we first present briefly the formalism underlying the derivation of this equation and of the cross section for dissociative attachment. For the detailed derivation itself, the reader is referred to Wadehra.[6]

Physically, one considers resonance formation to be possible when a molecule with N bound electrons interacts with an incident electron whose energy ε is such that a temporary stationary state of the $N+1$ electron system exists at the corresponding total energy. Within the Born-Oppenheimer approximation, the wave function of this resonant state can be expressed in the form $\phi(q,R\,)\xi(\mathbf{R})$, where ϕ is the electronic part and ξ is the nuclear part of the resonant wave function, q represents the totality of all electronic coordinates including those of the projectile, and ϕ depends only parametrically on R. The resonant state is embedded in a continuum of electronic states in which only N of the electrons are bound. A typical member of this continuum, corresponding to

nonresonant scattering, can be represented in the Born-Oppenheimer form $\psi_\varepsilon(q,R)\chi_{vJ}(\mathbf{R})$, where ε is the energy of the projectile electron, and v and J are the rovibrational quantum numbers of the target molecule. In both the continuum and discrete states, the electronic wave functions are of course completely antisymmetric with respect to the exchange of any two electrons. The total wave function of the system, then, consists of a discrete state interacting with a spectrum of continuum states:[3]

$$\Psi=\phi(q,R)\xi(\mathbf{R})+\int_0^\infty d\varepsilon\sum_{v,J} f_{vJ}(\varepsilon)\psi_\varepsilon(q,R)\chi_{vJ}(\mathbf{R}) , \qquad (1)$$

where the $f_{vJ}(\varepsilon)$ are expansion coefficients, and the sum runs over all the energetically accessible target rovibrational levels. It is worth pointing out that Eq. (1) contains the implicit assumption that only one resonant state need be considered; in the case of interest here (low-energy electrons on molecular hydrogen), this assumption is justifiably valid, as previous work has shown,[7] that the effects of the next higher-lying resonance, namely, the $B\,^2\Sigma_g^+$ resonance, are negligibly small for energies below 5 eV.

From the requirements that, first, the wave function Ψ is an eigenfunction of the total Hamiltonian H and, second, the continuum states over which the sum in Eq. (1) is taken represent outgoing waves except in the incident channel, one can show[6] that the nuclear wave function $\xi(\mathbf{R})$ satisfies the following integro-differential equation:

$$[T_N(\mathbf{R})+V^-(R)-E]\xi(\mathbf{R})=-V(E-E_{v_iJ_i},R)\chi_{v_iJ_i}(\mathbf{R})$$
$$-\int d\mathbf{R}'K(\mathbf{R},\mathbf{R}')\xi(\mathbf{R}') ,$$
$$(2)$$

with the kernel $K(\mathbf{R},\mathbf{R}')$ given by

$$K(\mathbf{R},\mathbf{R}')=\sum_{v,J}\chi_{vJ}^*(\mathbf{R}')\chi_{vJ}(\mathbf{R})$$
$$\times\lim_{\eta\to0+}\int_0^\infty d\varepsilon\frac{V^*(\varepsilon,R')V(\varepsilon,R)}{E-E_{vJ}-\varepsilon+i\eta} , \qquad (3)$$

where T_N is the kinetic energy of the nuclei, V^- is the effective potential energy in which they move in the resonant state, and E is the total energy of the interacting system. The quantity $V(\varepsilon,R)$ is referred to as the interaction matrix element; it represents the interaction between the discrete and continuum states and is of the form

$$V(\varepsilon,R)=\int dq\,\phi(q,R)H\psi_\varepsilon(q,R) , \qquad (4)$$

where the integration is over all the electronic coordinates.

It is sometimes convenient to express the nonlocal kernel in Eq. (3) explicitly in terms of its real and imaginary parts using Dirac's identity; thus

$$K(\mathbf{R},\mathbf{R}')=\sum_{v,J}\chi_{vJ}^*(\mathbf{R}')\chi_{vJ}(\mathbf{R})[\Delta(R',R,E-E_{vJ})$$
$$-\frac{i}{2}\Gamma(R',R,E-E_{vJ})] , \qquad (5)$$

with

$$\Delta(R',R,\varepsilon)=P\int_0^\infty d\varepsilon'\frac{V^*(\varepsilon',R')V(\varepsilon',R)}{\varepsilon-\varepsilon'} , \qquad (6)$$

and

$$\Gamma(R',R,\varepsilon)=2\pi V^*(\varepsilon,R')V(\varepsilon,R) .$$

The principal value integral $\Delta(R',R,\varepsilon)$ and the quantity $\Gamma(R',R,\varepsilon)$ represent nonlocal expressions for the level shift and level width, respectively.

In order to carry out the solution of the partial integro-differential equation (2), the first step is to separate out the radial part. This can be accomplished by decomposing $\xi(\mathbf{R})$ into partial waves and expressing the rovibrational state $\chi_{vJ}(\mathbf{R})$ in terms of its radial and angular parts:

$$\xi(\mathbf{R})=\sum_{J,m}\frac{\xi_{Jm}(R)}{R}Y_{Jm}(\hat{R}) ,$$

$$\chi_{vJ}(\mathbf{R})=\frac{\chi_{vJ}(R)}{R}Y_{Jm}(\hat{R}) .$$

Note that the same notation χ_{vJ} is used for both the total and radial vibrational wave functions. Substituting these expressions into Eq. (2) above, carrying out the angular integrations, and making use of the orthonormality of the Y_{Jm}'s, we find that $\xi_{Jm}(R)$ satisfies the one-dimensional equation

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2}+\frac{\hbar^2J(J+1)}{2MR^2}+V^-(R)-E\right]\xi_{Jm}(R)$$
$$=-\delta_{JJ_i}\delta_{mm_i}V(E-E_{v_iJ_i},R)\chi_{v_iJ_i}(R)$$
$$-\int_0^\infty dR'K_J(R,R')\xi_{Jm}(R') , \qquad (7)$$

with

$$K_J(R,R')=\sum_v\chi_{vJ}^*(R')\chi_{vJ}(R)$$
$$\times\lim_{\eta\to0+}\int_0^\infty d\varepsilon\frac{V^*(\varepsilon,R')V(\varepsilon,R)}{E-E_{vJ}-\varepsilon+i\eta} .$$

We shall not deal with transitions from one rotational level to another; thus, for our purposes, we can consider only the case $J=J_i$, $m=m_i$, and then omit the Kronecker δ's on the right-hand side of Eq. (7). For convenience we will refer to $\xi_{J_im_i}(R)$ as $\xi_i(R)$.

The solution of Eq. (7) is carried out by application of the technique presented in the Appendix for handling integro-differential equations of the form

$$\Lambda(R)\xi(R)=S(R)-\int_0^\infty dR'K(R,R')\xi(R')$$

[see Eq. (A1)], which applies when the kernel $K(R,R')$ can be expanded in terms of products of separate functions of R and R'. Direct application of this technique for computational purposes is complicated here by the dependence of $V(\varepsilon,R)$ in the kernel on the integration variable ε. We therefore specialize to the case where the

interaction matrix element can be expressed in the separable form

$$V(\varepsilon,R)=f(\varepsilon)F(R) ,$$

which allows us to factor out the integral over ε in the definition of $K_J(R,R')$ as an expansion coefficient. Putting

$$c_{vJ}=\lim_{\eta\to 0+}\int_0^\infty d\varepsilon\frac{|f(\varepsilon)|^2}{E-E_{vJ}-\varepsilon+i\eta} ,$$

and substituting for $K_J(R,R')$ explicitly, Eq. (7) becomes

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dR^2}+\frac{\hbar^2 J_i(J_i+1)}{2MR^2}+V^-(R)-E\right]\xi_i(R)$$

$$=-f(E-E_{v_iJ_i})F(R)\chi_{v_iJ_i}(R)$$

$$-\sum_v c_{vJ_i}\chi_{vJ_i}(R)F(R)$$

$$\times\int_0^\infty dR'\chi_{vJ_i}^*(R')F^*(R')\xi_i(R') .\quad(8)$$

The technique of the Appendix then lets us reduce Eq. (8) to a set of implicit equations for

$$D_v=\int_0^\infty dR\,\chi_{vJ_i}^*(R)F^*(R)\xi_i(R) .$$

If $G(R,R')$ is the Green's function for the operator on the left-hand side of Eq. (8), then the solution of Eq. (8) can be expressed as

$$\xi_i(R)=\int_0^\infty dR'G(R,R')F(R')\left[-f(E-E_{v_iJ_i})\chi_{v_iJ_i}(R')\right.$$

$$\left.-\sum_v c_{vJ_i}D_v\chi_{vJ_i}(R')\right] .$$

$$(9)$$

The D_v are determined by solving the matrix equation

$$\sum_{v'}G_{vv'}D_{v'}=s_v ,$$

where the $G_{vv'}$ and s_v are given by

$$G_{vv'}=c_{v'J_i}\int_0^\infty dR\int_0^\infty dR'\chi_{vJ_i}^*(R)F^*(R)$$

$$\times G(R,R')F(R')\chi_{v'J_i}(R')+\delta_{vv'} ,$$

$$s_v=-f(E-E_{v_iJ_i})\int_0^\infty dR\int_0^\infty dR'\chi_{vJ_i}^*(R)$$

$$\times F^*(R)G(R,R')F(R')$$

$$\times\chi_{v_iJ_i}(R') .$$

Substituting the solution for the D_v back into Eq. (9) then yields the solution for the nuclear wave function ξ_i in the resonant state.

We note in passing that the requirement that $V(\varepsilon,R)$ be expressible as a single separable term is not strictly necessary, and there are cases[2] where it is too restrictive. In general, the procedure presented here is applicable when the interaction matrix element $V(\varepsilon,R)$ can be expressed either as a single separable term or as a finite sum of separable terms.

III. SCATTERING MODEL
FOR MOLECULAR HYDROGEN

To obtain the local approximation to the theory presented above, one begins with Eq. (2) and replaces the quantity $E-E_{vJ}$ in the denominator on the right-hand side of Eq. (3) by the incident electron energy. The sum over open vibrational channels factors out, and a further assumption is made that the χ_{vJ} appearing therein form a complete set, so that it is permissible to replace the sum by the delta function $\delta(R-R')$. The resulting equation is

$$[T_N(\mathbf{R})+V^-(\mathbf{R})+\Delta(R)-(i/2)\Gamma(R)-E]\xi(\mathbf{R})$$

$$=-V(E-E_{v_iJ_i},R)\chi_{v_iJ_i}(\mathbf{R}) ,$$

where the width $\Gamma(R)$ is related to the interaction matrix element $V(\varepsilon,R)$ as

$$\Gamma(R)=2\pi|V(\varepsilon,R)|^2 ,\quad(10)$$

and the level shift $\Delta(R)$ is essentially the Hilbert transform of the width $\Gamma(R)$. This ordinary differential equation has been solved previously for the e-H_2 system, and the corresponding results for attachment cross sections have been presented in detail.[1,8]

One of the principal aims of the present work is to study nonlocal effects in dissociative attachment to H_2. We have tried, as much as possible, to isolate those features which appear in our nonlocal cross sections, but are absent in their local counterparts. At the same time, we have tried to facilitate comparison with earlier results by keeping our model for the potential curves of H_2 and H_2^- as close as possible to that used in our previous work.[1,8] Nevertheless, we have not insisted upon this dogmatically where we felt it would be unreasonable to do so. Since we shall be presenting both completely new nonlocal cross sections and recently computed local cross sections for comparison, it is important to understand how these results are related to each other, as well as to the (local) results obtained earlier. Therefore, we now examine in greater detail the potentials, widths, and interaction matrix elements used in our present computations.

For scattering of low-energy (≤ 5 eV) electrons, it is sufficient to consider only the $X\,^2\Sigma_u^+$ resonance of H_2^-, which decays by electron emission to the ground state of neutral H_2. The reasons for not considering the $B\,^2\Sigma_g^+$ resonance, which becomes important at higher energies,[7] are twofold: first, because our choice of form for partial decay width is strictly correct only near threshold and, second, because this resonance decays primarily to the repulsive $b\,^3\Sigma_u^+$ state of H_2. Our nonlocal calculations of cross sections at energies greater than 0.75 eV above threshold implicitly ignore the possibility in which the electron is autodetached and the molecule H_2 is left in one of the continuum states of the ground electronic state.

The potential curves chosen for the neutral and resonant states are unchanged from those used previously.[1,8] Briefly, our potential curve $V_0(R)$ for the ground state of neutral H_2 was drawn from the work of Kolos and Wolniewicz[9] and joined to a suitable asymptotic form for

values of the internuclear separations larger than 8 a.u.; while for $V^-(R)$, the real part of the potential curve of the $X\,^2\Sigma_u^+$ resonance of H_2^-, the following form is chosen:

$$V^-(R)=V_0(R)-A+\alpha\exp(-\beta R^2)\ ,$$

where A is the electron affinity of atomic hydrogen, and the constants α and β are determined in a semiempirical manner.[1] The level shift $\Delta(R',R,\varepsilon)$ of Eq. (6) is a nonlocal function whose local approximation $\Delta(R)$ simply adds on to $V^-(R)$, the potential curve of the resonant state, in the local approximation [see Eq. (10)]. Now since the potential curve $V^-(R)$ is determined semiempirically, a partial contribution of the level shift is included in $V^-(R)$. For the decay width $\Gamma(R)$, we chose the form

$$\Gamma(R)=Ck_u^3(R)\ ,$$

suitable for a p-wave resonance near threshold, where

$$\frac{\hbar^2 k_u^2(R)}{2m_e}=V^-(R)-V_0(R)$$

represents the energy of an electron captured at the internuclear separation R. The constant C was chosen to make the nonlocal attachment cross section for H_2 at 3.75 eV equal to 1.6×10^{-21} cm^2. This value of the attachment cross section, reproduced by the value of C equal to 2.884 a.u., is obtained, according to an analysis by Schulz and Asundi,[10] by comparing the laboratory negative ion currents near 3.75 and 14.2 eV and then using the experimental cross section of Rapp, Sharp, and Briglia[11] at 14.2 eV. By a similar analysis, the H^- formation cross section at 3.75 eV would be 2.8×10^{-21} cm^2 if the negative-ion currents near 3.75 and 14 eV were compared and the experimental cross sections of Schulz[12] were used at 14 eV. The value of C required to reproduce this value (2.8×10^{-21} cm^2) of the H^- from the H_2 cross section is 2.59 a.u. The former value of C was preferred over the latter by an analysis of the isotope effect;[1] it is worth adding, however, that neither value of C gives good agreement with the experimental value of the "isotope ratio" $\sigma(H_2)/\sigma(HD)$ at threshold, and the value of C needed to reproduce the required value ($\cong6.5$) of the isotope ratio would drive down the threshold attachment cross section for H_2 by 2 orders of magnitude. Finally, the interaction matrix element $V(\varepsilon,R)$ was obtained from $\Gamma(R)$ according to the relationship (10).

Both the Green's function and the neutral molecule's bound-vibrational-level wave functions were obtained by numerically solving the Schrödinger equation using the Numerov method. The matrix elements $G_{vv'}$ and all related integrals were evaluated using Simpson's rule. The relation

$$-\frac{\hbar^2 K}{2M}\lim_{R\to\infty}|\xi_i(R)|^2=\mathrm{Im}\left[f^*(\varepsilon_i)D_{v_i}+\sum_v c_{vJ_i}^*|D_v|^2\right]\ ,$$

$$(11)$$

which can be derived by multiplying Eq. (8) by $\xi_i^*(R)$, subtracting the complex conjugate of the resulting equation, and integrating both sides over all values of R, was used as a consistency check on our nonlocal results and also to guide the choice of the numerical step size for integration. Here K is the wave number of the relative motion of ion-atom pairs in the final channel of the attachment process and $\varepsilon_i=E-E_{v_iJ_i}$ is the energy of the incident electron. A relation analogous to Eq. (11), presented earlier[1] and derived in a similar way, was used to check the consistency of the results in the local theory.

Finally, if the target molecule is homonuclear, the total cross section for negative-ion production through dissociative attachment is given by

$$\sigma_{DA}=\frac{2\pi^2 m_e}{k}\frac{K}{M}\lim_{R\to\infty}|\xi_i(R)|^2\ ,\qquad(12)$$

where k is the wave number of the incident electron. Here the electronic part of the wave function is assumed to be momentum normalized. For heteronuclear isotopes, such as HD where an equal probability exists for the formation of either H^- or D^-, the experimental attachment cross section is obtained by observing the current of any one of the two negative-ion species. The theoretical attachment cross section which should be compared with this experimental cross section is then obtained from Eq. (12) by multiplying with a factor of 0.5.

IV. RESULTS AND DISCUSSION

Before comparing our calculated cross sections for dissociative electron attachment to H_2 and its isotopes with the corresponding experimental cross sections, we briefly review some of the available experimental data. Even though the formation of H^- by attachment of electrons, with energies greater than 5 eV, to H_2 had been observed previously,[11–13] the first experiment to show clearly the formation of H^- by the impact of electrons, with energies in the range 3.75–5 eV, to H_2 was by Schultz and Asundi.[14] In a later paper,[10] these investigators provided experimental cross sections for the formation of both H^- and D^- from H_2, HD, and D_2 for electrons in the energy range 3.75–5 eV. A rather significant isotope effect observed in the attachment cross sections provided information about the lifetimes of the relevant resonances of H_2^-. Subsequently, the effect of the initial rotational and vibrational excitation of H_2 on the attachment cross sections was investigated, and it was found to be very dramatic.[15,16] A large increase, more than an order of magnitude, in the attachment cross section was observed when H_2 was initially excited from the $v=0$ to 1 level. Finally, the angular distributions of H^-, which were determined by observing the differential cross sections for dissociative attachment of 3.75–13 eV electrons to H_2, were analyzed successfully by using a purely resonant scattering theory.[17]

Figure 1 shows the total cross sections, obtained using the nonlocal theory, for production of H^- through dissociative attachment to H_2 in the lowest rovibrational level, compared with experimental data taken from Schulz and Asundi.[10] Agreement between theory and experiment is particularly good in the range of electron energies be-
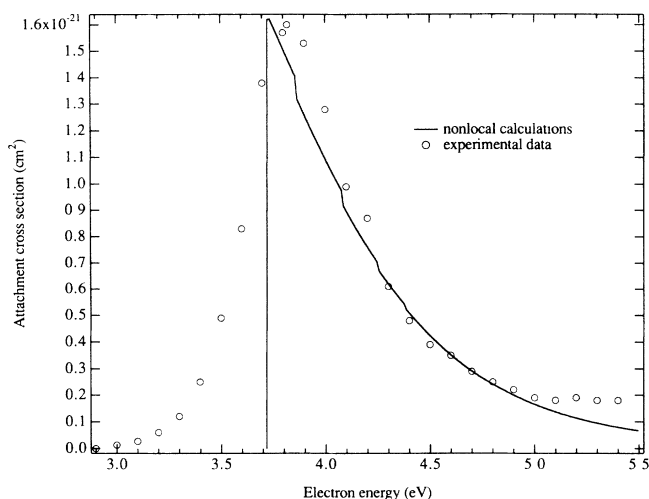
FIG. 1. Cross sections for H^- production from H_2. The solid curve represents the nonlocal theory; the circles represent experimental data from Schulz and Asundi (Ref. 10).

FIG. 3. Cross sections for D^- production from D_2. The solid curve represents the nonlocal theory; the circles represent experimental data from Schulz and Asundi (Ref. 10).

tween 4.5 and 5.0 eV, which indicates that our width, although derived using Wigner's[18] threshold law, is nonetheless reasonably accurate over a wide range of incident energies. Figures 2 and 3 similarly display the cross sections for production of D^- from HD and from D_2 in their lowest rovibrational level, respectively. The theoretical cross sections for D^- from HD agree to within 10% with their experimental counterparts for all electron energies except very near the peak, where the discrepancy is closer to 40%, while the best agreement is once again between 4.5 and 5.0 eV. Only in the case of D^- from D_2 do we find a dramatic departure, almost by a factor of 3 near threshold, of the theoretical cross sections from the experimental data. The reason for this discrepancy is unclear, but it could possibly be related to
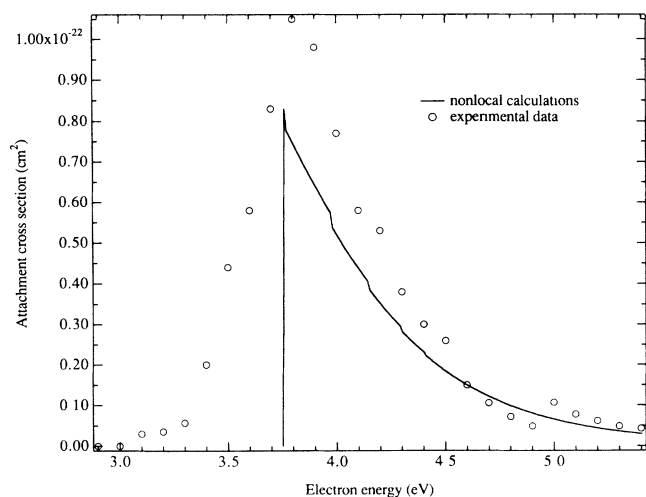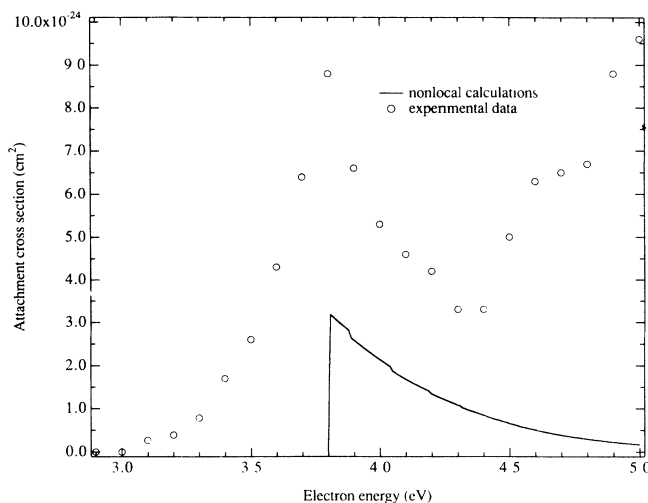
a sharp rise in the experimentally observed D^- signal for energies at and above 4.4 eV. Schulz[19] has proposed that this sharp rise in the D^- current may be partly due to excitation of the higher-lying $B\,{}^2\Sigma_g^+$ resonance at these energies. This proposal, however, appears to be inconsistent with the isotopic dependence observed in the experimental attachment cross sections[11] for electron energies above 8 eV, where the ${}^2\Sigma_g^+$ resonance dominates.

In Fig. 4 we compare the nonlocal cross section for attachment to H_2 in the $J=0$, $v=0$ level to its local counterpart. It can be seen that the difference between the two cross sections at a given energy is small, on the order of 10% near threshold where the difference is largest. That the nonlocal cross section is larger than the local one reflects the fact that in the local calculation, all vibra-
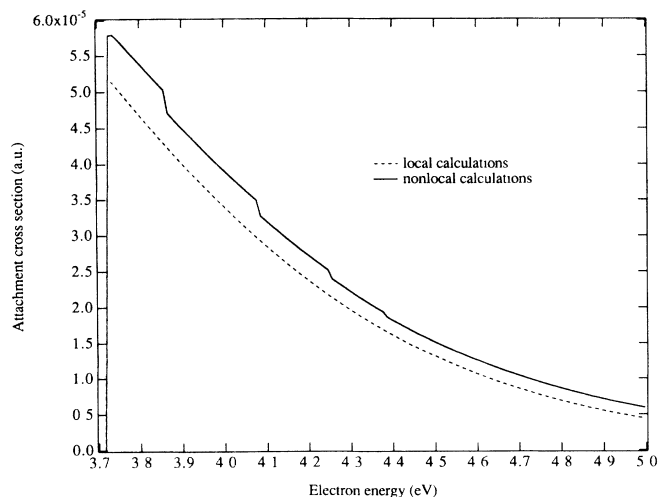

FIG. 2. Cross sections for D^- production from HD. The solid curve represents the nonlocal theory; the circles represent experimental data from Schulz and Asundi (Ref. 10).

FIG. 4. Local and nonlocal cross sections for attachment to H_2 in the lowest rovibrational level.

tional channels are considered to be open, whether or not they are actually energetically accessible. The two cross-section curves evidently do not merge into each other even at higher energies because, in our calculation, excitation of the continuum levels (corresponding to $H+H+e$) was not taken into account.

The most significant difference between the local and nonlocal cross sections is the conspicuous step structure in the nonlocal cross section in the energy range below about 4.5 eV. This step structure could not be clearly seen in the available experimental data since the energy resolution of the apparatus used was of the order of 0.1 eV. These steps occur at energies for which a new vibrational channel opens up. Thus, for example, the first step in the cross section for attachment to H_2 in $v=0$, $J=0$ level at about 3.83 eV corresponds to the opening of the $v=10$ channel, while the last is at 4.39 eV, where the $v=13$ level becomes energetically accessible. It might be tempting to attribute the loss of attachment flux at these steps merely to diversion into the newly opened vibrational channel, but Fig. 5 shows that this is an oversimplification. The opening of a new vibrational level is accompanied by upward jumps in the cross sections for the vibrational excitation of previously open channels. The magnitude of the upward jumps becomes smaller as we consider levels farther removed in energy from the newly opened level. Threshold anomalies of this kind have been studied theoretically by Wigner,[18] and some investigators[20] report having observed such phenomena experimentally in inelastic electron-atom scattering processes. Here the sum of all discontinuities, including both in the dissociative attachment and in the vibrational excitation cross sections, is indeed zero, as can be seen by considering the consistency relation [Eq. (11)] for the nuclear wave function $\xi(\mathbf{R})$. This consistency relation is
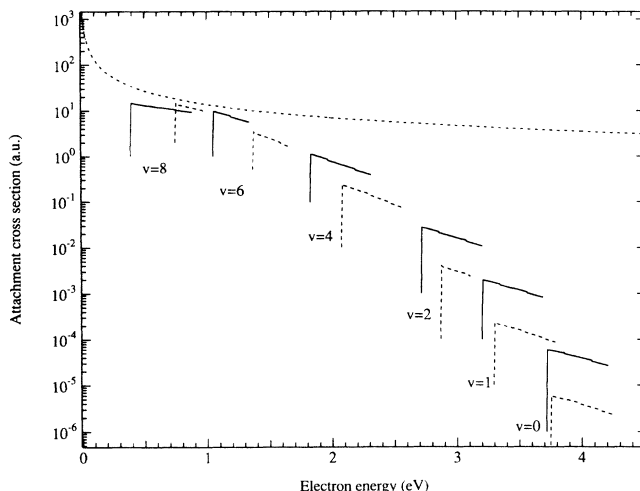
FIG. 6. Total cross sections for attachment to H_2 (solid curves) and HD (dashed curves) in various rotationless vibrational levels. The dot-dashed curve on the top represents an upper bound provided by $1/k^2$, where $\hbar^2 k^2/2m_e$ is the energy of the incident electron.

satisfied in our present calculations for H_2 out to at least three significant figures. The left-hand side of this relation is obviously proportional to the attachment cross section, while the term corresponding to a given v in the sum on the right-hand side is related to the cross section for exciting the molecule to the vth vibrational level. The first term on the right-hand side of Eq. (11) changes slowly as a function of the incident electron energy, and its first derivative appears everywhere to be continuous; therefore, it does not appear to contribute to the step structure. The disappearance of the step structure in the local treatment is not very surprising since the local approximation entails replacing the quantity $E-E_{vJ}$ in the denominator on the right-hand side of Eq. (3) by the incident electron energy and assuming that the set of vibrational levels over which one sums can be regarded as complete; naturally, in such an approximation all sensitivity to the number of open channels is washed out.

Finally, in Fig. 6 we display the peak total attachment cross sections for various rotationless levels of H_2 and HD against electron energy on a logarithmic plot. The dot-dashed curve on the top represents $1/k^2$, which is seen to provide an upper bound to the attachment cross sections for all six isotopes of H_2 for all values of the incident electron energies considered. This is consistent with an observation of Gauyacq[21] that the dissociative attachment cross section is of the form

$$\sigma_{DA}(k)=\frac{\pi}{k^2}P_{det}(k)\ ,$$

where $P_{det}(k)$, representing the probability that the electron does not autodetach in the resonant state, is less than unity. In fact, $1/k^2$ provides a tighter upper bound than π/k^2.

To summarize, our nonlocal attachment cross sections agree reasonably well with the experimental observations

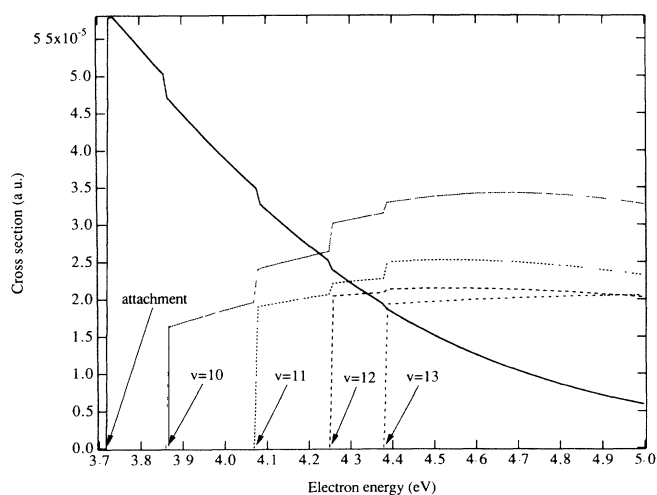

FIG. 5. Various nonlocal cross sections for scattering from the lowest rovibrational level of H_2, including that for dissociative attachment and those for excitation of the $v=10$ to 13 levels. The cross sections for vibrational excitation of $v=10$, 11, 12, and 13 levels are multiplied by factors of 15, 25, 50, and 100, respectively.

for H_2 and HD. The reasons for the discrepancy between theory and experiment in D_2 are unclear, especially near threshold, and we feel further investigation is warranted, both theoretical and experimental. The step structure evident in our attachment cross sections is an intrinsic feature of the nonlocal theory, whose confirmation or refutation awaits experimental attachment cross sections with higher-energy resolution ($\cong 0.01$ eV) than currently available.

ACKNOWLEDGMENTS

APPENDIX: SOLUTION
OF AN INTEGRO-DIFFERENTIAL EQUATION

Consider an integro-differential equation of the form

$$\Lambda(R)\xi(R) = S(R) - \int_0^\infty dR' K(R,R')\xi(R') , \quad (A1)$$

where $\xi(R)$ is the unknown function, Λ is a linear differential operator, $S(R)$ is the "source" term, and $K(R,R')$ is the kernel. We shall assume that there exists a Green's function $G(R,R')$ for the operator Λ, so that the solution to (A1) can be written as

$$\xi(R) = \int_0^\infty dR' G(R,R')$$
$$\times \left[S(R') - \int_0^\infty dR'' K(R',R'')\xi(R'') \right] .$$
$$(A2)$$

Our technique for solving equations of this kind applies when the kernel is expressible in the separable form

$$K(R,R') = \sum_{v=0}^N c_v p_v(R) q_v(R') . \quad (A3)$$

In this case, defining the quantity

$$D_v = \int_0^\infty dR \, q_v(R)\xi(R) \quad (A4)$$

allows us to write the solution (A2) in a more manageable form:

$$\xi(R) = \int_0^\infty dR' G(R,R') \left[S(R') - \sum_{v=0}^N c_v p_v(R')D_v \right] . \ (A5)$$

If we multiply both sides of (A5) by $q_v(R)$ and integrate over R, we obtain an implicit equation:

$$D_v = \int_0^\infty dR \int_0^\infty dR' q_v(R)G(R,R')$$
$$\times \left[S(R') - \sum_{v'=0}^N c_{v'}p_{v'}(R')D_{v'} \right] , \quad (A6)$$

for the elements D_v of a column matrix. This equation can be put in an explicit form if we define the elements of two-dimensional matrices

$$g_{vv'} = \int_0^\infty dR \int_0^\infty dR' q_v(R)G(R,R')p_{v'}(R') , \quad (A7)$$

and

$$G_{vv'} = c_{v'}g_{vv'} + \delta_{vv'} , \quad (A8)$$

and the column matrix

$$s_v = \int_0^\infty dR \int_0^\infty dR' q_v(R)G(R,R')S(R') . \quad (A9)$$

With these definitions (A6) becomes

$$\sum_{v'=0}^N G_{vv'}D_{v'} = s_v , \quad (A10)$$

and the problem of solving (A1) for $\xi(R)$ has been reduced to that of computing the matrix elements $g_{vv'}$ and s_v, solving (A10) for the D_v, and then substituting the resulting values into (A5).

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