PHYSICAL REVIEW VOLUME 143, NUMBER 1 MARCH 1966

Proton–Hydrogen-Atom System at Large Distances. Resonant Charge Transfer and the $1s\sigma_g$-$2p\sigma_u$ Eigenenergies of H_2^+†

JAMES M. PEEK
Sandia Laboratory, Albuquerque, New Mexico

(Received 11 October 1965)

The resonant charge-transfer reaction of a proton with a hydrogen atom is evaluated in the adiabatic approximation. Previous calculations of this cross section have used various approximations to the energy difference between the $1s\sigma_g$ and $2p\sigma_u$ states of the hydrogen molecule ion H_2^+. This approximation is removed by solving the H_2^+ Schrödinger equation for the eigenparameters required in addition to those previously available in the literature. The resulting energy differences, found for internuclear separations of $R\leq 40.0a_0$, are used to test the accuracy of large R estimates based on quasiclassical (WKB) and asymptotic arguments. The charge-transfer cross section calculated with the eigenenergies is found to be, at most, a few percent different from earlier results based on approximate energy differences. Firsov's approximation and a recent modification by Smirnov are shown to be highly accurate when used with the eigenenergies.

I. INTRODUCTION

In this paper we consider the charge-transfer reaction

$$H^+ + H(1s) = H(1s) + H^+, \tag{1}$$

which is a symmetrical and resonant process. A number of theoretical treatments of this problem have been documented. One result gives the total cross section as

$$\sigma = 2\pi \int_0^\infty \rho \sin^2(x/v) d\rho, \tag{2}$$

where

$$x(\rho) = \tfrac{1}{2} \int_{-\infty}^{\infty} \Delta E \, dz, \tag{3}$$

$$\Delta E = E(2p\sigma_u) - E(1s\sigma_g). \tag{4}$$

These formulas are restricted to collisions with small relative velocities v and, in the framework of the impact-parameter method,[1] correspond to a two-state expansion in the hydrogen molecule ion (H_2^+) wave functions when momentum transfer is neglected. The energies required by Eq. (4) are the electron eigenenergies of the $2p\sigma_u$ and $1s\sigma_g$ states of H_2^+, respectively, calculated with the Born-Oppenheimer separation of electronic and nuclear variables. The integral in Eq. (3) is evaluated for straight-line trajectories, along z, with a distance of closest approach for the protons of ρ.

Heretofore the evaluation of Eqs. (2) and (3) has been accomplished by the use of various approximations to the required energy difference ΔE. Because of the relative simplicity of the system defined by Eq. (1), it is feasible to remove the approximation to ΔE by solving the H_2^+ electron Schrödinger equation. The eigenvalues required in addition to those already available in the literature have been calculated. Details of this calculation are available elsewhere[2,3] and just the data pertinent to the charge-transfer problem are reported in Sec. II. A comparison of the resulting energy differences with two types of asymptotic estimates of ΔE is given. Cross sections calculated with these new energy differences and a comparison with similar calculations are given in Sec. III. The technique developed by Firsov,[4] which relies only on large R energy differences, and a recent modification by Smirnov[5] are discussed.

II. H_2^+ EIGENENERGIES

If one assumes the Born-Oppenheimer separation of nuclear and electronic variables for H_2^+, the resulting electron Schrödinger equation can be solved to any predetermined accuracy (at least in principle) by relatively simple techniques. The most extensive tabulation of electron eigenparameters for this system is given by Bates, Ledsham, and Stewart.[6] Wallis and Hulburt[7] tabulate the eigenparameters for several states, but they only consider a few widely spaced values of R. Wind[8] gives an extensive tabulation of the potential-energy curve for the ground state, $H_2^+(1s\sigma_g)$, and has also completed a similar calculation[9] for the first excited electronic state, $H_2^+(2p\sigma_u)$. These calculations, motivated by problems in molecular structure, do not provide adequate information for the solution of the proton–hydrogen-atom charge-transfer problem for two reasons. First, since it has been demonstrated[10] that Eqs. (2) and (3) are valid only for collision energies less than 10 keV, large impact

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† This work was supported by the U. S. Atomic Energy Commission.

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[5] B. M. Smirnov, Zh. Eksperim. i Teor Fiz. 46, 1017 (1964) [English transl.: Soviet Phys.—JETP 19, 692 (1964)].

[6] D. R. Bates, Kathleen Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) A246, 215 (1953).

[7] R. F. Wallis and H. M. Hulburt, J. Chem. Phys. 22, 774 (1954).

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[10] A. F. Ferguson, Proc. Roy. Soc. (London) A264, 540 (1961).

parameters ρ play an important role in the charge transfer cross section in the energy range for which this theory is applicable. Hence, knowledge of ΔE for rather large R is necessary for the evaluation of the integral occurring in Eq. (3). Second, the $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+ become degenerate for infinite R, and it is known that ΔE decreases exponentially as R increases when R is large. As a consequence, it is necessary to know the eigenenergies at large R with high accuracy because of the cancellation of significant figures when computing ΔE from Eq. (4).

The eigenenergies for the required range of R have been computed to the necessary accuracy on a CDC 3600 digital computer by use of double-precision techniques. The details of this calculation are reported elsewhere.[2,3] Reference 3 contains the eigenparameters for the $1s\sigma_g$ and $2p\sigma_u$ states for $R=0.1(0.01)1.00(0.05)30.0$ a_0 and, using the procedure described in this reference, this calculation has been extended to 40.0 a_0. The step size of 0.05 a_0 for the larger R was chosen to facilitate the evaluation of Eq. (3). A resume of these data is given in Table I. All quantities are in (Hartree) atomic units unless specified otherwise. For comparison, two types of estimates of ΔE are also given. The estimate labeled ΔE(H) was obtained from the first term of a formula given by Holstein.[11] The technique used to derive this formula relied on the WKB approximation; a similar calculation has been reported by Smirnov.[5] The results labeled ΔE(OS) are from a formula derived by Ovchinnikov and Sukhanov[12] (OS). These authors solve the H_2^+ eigenvalue problem for large R directly by use of asymptotic techniques. The first term of their result is identical to the first term obtained by the WKB argument,[5,11] $\Delta E=(4R/e)\exp(-R)$, but higher terms of the two methods differ. The agreement of the present results with the OS formula, plus the fact that the remainder estimate for the OS results, $O[R^{-2}\exp(-R)]$, is consistent with the differences in the two calculations, indicates that only the first term of the available results based on the WKB argument is correct.

TABLE I. The $2p\sigma_u$-$1s\sigma_g$ energy differences in Hartree atomic units for several internuclear separations, in units of a_0. The values of ΔE were calculated from the eigenenergies, ΔE(H) is from the first term of a formula given by Holstein,[a] and ΔE(OS) is from an estimate by Ovchinnikov and Sukhanov.[b]

R	ΔE	ΔE(H)	ΔE(OS)
5	4.7129(−2)[c]	4.9575(−2)[c]	4.8336(−2)[c]
10	6.7766(−4)	6.6807(−4)	6.8060(−4)
15	6.8761(−6)	6.7521(−6)	6.8834(−6)
20	6.1678(−8)	6.0661(−8)	6.1703(−8)
25	5.1847(−10)	5.1091(−10)	5.1857(−10)
30	4.1850(−12)	4.1311(−12)	4.1856(−12)
35	3.2852(−14)	3.2473(−14)	3.2855(−14)
40	2.5269(−16)	2.5006(−16)	2.5270(−16)

[a] Reference 11.
[b] Reference 12.
[c] The number in parenthesis following each ΔE is the power of ten by which that entry must be multiplied.

III. THE CHARGE-TRANSFER CROSS SECTION

The charge-transfer cross section for the process defined by Eq. (1) is given in Table II for several collision velocities v. Equation (3) was evaluated using a Tchebichef quadrature formula with ΔE computed from the eigenenergies for $R\leq 40.0$ a_0 and from the OS formula for $R>40.0$ a_0. The total cross section, given by Eq. (2), was then evaluated using Simpson's rule. The same numerical procedure was also used, in conjunction with the linear combination of atomic orbitals (LCAO) energy difference, to calculate this cross section, and these data are included in Table II for purposes of comparison. The use of the LCAO energy difference corresponds to an expansion in the isolated atomic wave functions rather than in the (molecular) wave functions of the entire scattering system.

A number of calculations of this cross section have been reported in the literature which differ from the present results only in that approximations to ΔE were used. To assess the effect of using ΔE as calculated from the molecular eigenvalues the following comparisons are made. The LCAO energy differences have been used by Dalgarno and Yadav,[13] McCarroll,[14] and Gurnee and Magee.[15] The LCAO calculation reported

TABLE II. The charge-transfer cross section for several collision velocities; the velocity is in units of the electron velocity of the innermost Bohr orbit. The first column of cross sections was calculated with the eigenenergies, the second with the LCAO energy difference, the third with Firsov's[a] approximation and the last with Smirnov's[b] approximation. The Firsov and Smirnov results are to be compared with the eigenvalue calculation.

	$\sigma(\pi a_0^2)$			
v	Eigen-energies	LACO	Firsov	Smirnov
0.01	50.12	48.40	49.0	50.3
0.015	45.40	43.94		
0.02	42.21	40.79	41.1	42.4
0.03	37.85	36.51		
0.05	32.65	31.38		
0.07	29.38	28.17		
0.10	26.10	24.93		
0.20	20.03	19.02	19.5	20.3
0.40	14.49	13.68		
0.50	12.70	11.96		
0.60	11.22	10.64		

[a] Reference 4.
[b] Reference 5.

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[11] T. Holstein, Westinghouse Research Report No. 60-94698-3-R9, 1955 (unpublished).

[12] A. A. Ovchinnikov and A. D. Sukhanov, Dokl. Akad. Nauk SSSR **157**, 1092 (1964) [English transl.: Soviet Phys.—Doklady **9**, 685 (1965)].

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[14] R. McCarroll, Proc. Roy. Soc. (London) **A264**, 547 (1961).

[15] E. F. Gurnee and J. L. Magee, J. Chem. Phys. **26**, 1237 (1957).

here overlaps McCarroll's calculation for the higher energies and represents an extension for $v \leq 0.05$. The data given here only correspond to his tabulated points for $v=0.2$; however, the calculation of additional points in common with his tabulation by the present numerical techniques also gave good agreement. Of the two energies considered by Gurnee and Magee, the higher energy point is in good agreement with the present LCAO results and their lower point is consistent with the extrapolation of the LCAO data. Dalgarno and Yadav actually consider a wave formulation of the problem. However, they use LCAO energies and for the velocities considered here their results should be comparable to the LCAO data given in Table II. For energies less than 1 keV the agreement between these two calculations is good. Bates and Boyd[16] obtain ΔE from the eigenenergies[6] for $R \leq 9.0\ a_0$ and use an approximate formula for $R > 9.0\ a_0$. Their results for relative collision energies of 10 eV or less are between the calculation based on the eigenvalues and the one using the LCAO energy differences, being somewhat closer to the LCAO results. Ferguson's[10] curve, given only for energies greater than 1.0 keV, appears to be below the eigenvalue calculation by about 1%, but this difference could be attributed to inaccuracies in reading his graph. He uses a form of variational wave functions investigated by Dalgarno and Poots[17] and presumably his energy difference is based on these wave functions. Boyd and Dalgarno[18] use an analytic fit to energy differences obtained from the eigenvalue calculations of Bates, Ledsham, and Stewart[6] and Wallis and Hulburt.[7] Their graphical results, for energies between 1.0 and 100 eV, appear equidistant between the LCAO and eigenvalue calculations given here.

The well-known treatment of Eqs. (2) and (3) by Firsov[4] has recently been modified by Smirnov[5] and applied to the reaction under consideration here. Their approach, with the condition of small v, has the distinct advantage of just requiring $x(\rho)$ for large ρ and avoids the quadrature required by Eq. (2). Calculations by both formulas,[19] based on the ΔE obtained from the eigenenergies, are included in Table II. As observed by Bates and Boyd[16] for cases in which $\Delta E \propto R^{-n}$, these formulas prove quite effective.

The removal of any assumption concerning ΔE in the evaluation of Eq. (3) indicates that errors of only a few percent are introduced when carefully considered approximations to ΔE are used. Cross sections based on the LCAO and eigenvalue energy differences are found to differ in this case by 5% and cross sections based on various approximations to ΔE are observed to be bounded by these two calculations. It has also been demonstrated that techniques in the spirit of Firsov's evaluation of the cross section are reliable when used with ΔE obtained from the eigenenergies. Since this approximation only requires ΔE for large R, where quasiclassical[5,11] or asymptotic[12] arguments are useful, it appears that accurate treatment of charge-transfer reactions by this theory should be possible for systems of such complexity that there is little hope of solving the Schrödinger equation for ΔE.

ACKNOWLEDGMENTS

The author is indebted to Thomas A. Green for bringing attention to this problem and for his many stimulating discussions and to Mrs. Marcella Madsen for her invaluable assistance in programming the digital computer.

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[18] T. J. M. Boyd and A. Dalgarno, Proc. Phys. Soc. (London) **A72**, 694 (1958).

[19] It should be noted that the curve given by Smirnov is considerably higher than the values listed in Table II as being calculated with his formula. This presumably is accounted for by retaining unjustified terms in his estimate of ΔE (see the discussion in Sec. II). Had he used just the first term in his formula for ΔE, he would have obtained results rather close to the calculation based on the eigenenergies.