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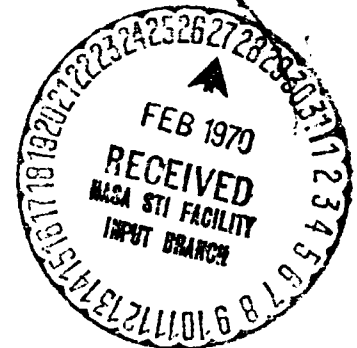
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ELECTRON EXCHANGE IN H-H COLLISIONS: THE HEITLER-LONDON CURVES AS A FUNCTION OF INTERNUCLEAR DISTANCE AND VELOCITY

A. B. RITCHIE

JANUARY 1970



GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

N70-19232

(ACCESSION NUMBER)

(THRU)

(PAGES)

(CODE)

TMX 63823

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

Electron Exchange in H-H Collisions: The Heitler London Curves
as a Function of Internuclear Distance and Velocity

Burke Ritchie^{*}

Laboratory for Theoretical Studies, National Aeronautics and Space
Administration, Goddard Space Flight Center, Greenbelt, Maryland 20771

^{*} NRC-NASA Resident Research Associate

Abstract

The Heitler-London curves for the interaction of two hydrogen atoms are calculated as a function of the internuclear distance and velocity. Electron exchange terms are found to dominate the interaction energy at laboratory energy 1 kev, to be quite significant at 25 kev, and to be negligible at 400 kev. The exchange energy is attractive at 25 kev and below, but at 100 kev it is repulsive. Hence in going from 25 to 100 kev the Singlet and Triplet curves go from attractive and repulsive to repulsive and attractive, respectively, suggesting that an oscillatory behavior of the cross-section versus energy is possible. These results have important implications for the calculation of atom-atom excitation cross-sections in this energy range.

Introduction

Recently there have been a number of experimental¹ and theoretical² papers on ion-atom collisions and Lyman- α production and polarization. Activity has also begun in the understanding of neutral-neutral collisions^{3,4} and the theory⁵ of heavy particle scattering in general. Theoretically both systems are subject to the difficulty that for a larger than two-electron system the electronic wave function at zero velocity of the nuclei is either unknown (the wave function for H^+-H is known exactly and to a degree of accuracy which is virtually exact for $H-H$ ⁶) or known only in the interior, molecular binding regions for certain selected molecular symmetries (for three or more heavy bodies) to degrees of accuracy which may permit the calculation of elastic or target excitation of rotation-vibration states scattering but which do not permit the study of chemical reactions⁷, and unknown entirely in the region of intermediate internuclear separation. Added to these difficulties of wave function ignorance is the fact that adiabatic states calculated in a molecule fixed frame are not correct with respect to the center of mass frame at infinity⁸ and must be transformed into the correct asymptotic states⁹.

An intermediate approach to the heavy particle scattering problem would be to divide the molecular space into the interior region for which accurate molecular states would be required and the intermediate-asymptotic region whose physics can be described by use of the states of the separated systems which

are properly anti-symmetrized to account for the identity of the electrons, which becomes important in the region of small overlap, i.e. the unknown "intermediate" region. This is just the Heitler-London¹⁰ wave function whose exchange property permitted the first qualitative calculation of the binding energy of the hydrogen molecule. Once they become available the accurate, interior functions can be fitted to the Heitler-London functions in the intermediate region. Since the Heitler-London functions are the correct states at infinity such a fitting would be equivalent to the transformation of molecular states into correct asymptotic states at infinity⁹, and in addition since the fitting could be performed before infinity, while the interaction was still on but weak, the physics of this region would be known.

Theory and Numerical Procedures

Recently Flannery¹¹ has calculated H-H 1s1s-1s2s excitation cross-sections in the coupled atomic state impact parameter picture. Electron exchange is not considered, and the set of direct product states used are precisely those of the van der Waals region in which there is no overlap. Qualitatively one would expect overlap to be important at close enough encounters to produce an excitation of one of the atoms. The justification usually given is that at high proton velocities the time needed for the electrons to become nonlocalized in the two-center, molecular space is not available. In this paper we calculate

the diagonal exchange matrix element,

$$H_i(R, v) = R e < |s(1A)|s(2B)| (R^{-1} - r_{1B}^{-1} - r_{2A}^{-1} + r_{12}^{-1}) | |s(1B)|s(2A) >, \\ |s(1A) = \pi^{-\frac{1}{2}} e^{-r_{1A}} e^{-i \underline{v} \cdot \underline{r}_1} \\ |s(1B) = \pi^{-\frac{1}{2}} e^{-r_{1B}} e^{i \underline{v} \cdot \underline{r}_1} \quad (1)$$

where \underline{v} is the relative velocity vector, of magnitude $\frac{1}{2}$ the laboratory velocity, and protons A and B are going in the directions of negative and positive velocities respectively. For mathematical simplicity we consider the special case of zero impact parameter ($b=0$, where $R=(b^2+(vt)^2)^{\frac{1}{2}}$ in the rectilinear trajectory picture) corresponding to a head-on collision. This avoids the m coupling in the integral over the product containing $r_{12}^{-1} \exp(i \underline{v} \cdot \underline{r})$, because \underline{v} is taken along the polar axis. Then we can write,

$$e^{i \underline{v} \cdot \underline{r}} = e^{i v \frac{R}{2} \xi \eta} = \sum_{k=0}^{\infty} (i)^k (2k+1) j_k(v \frac{R}{2} \xi) P_k(\eta) \quad (2)$$

where $j_k(vR/2\xi)$ is the spherical Bessel function and $P_k(\eta)$ the Legendre polynomial. The overlap and nuclear attraction integrals are straightforwardly integrated numerically; and a check with the known results¹² for zero velocity shows agreement to six decimal places. The electron-electron repulsion integrals are more difficult. Use of the Neumann expansion¹³ for r_{12}^{-1} results in an infinite series in partial k "waves" because of the coupling of the Legendre polynomials

In the Neumann expansion with those in the plane wave expansion (2). It was found that for v (laboratory velocity) $= .2$ (for $v=0$ only the $k=0$ and $k=2$ waves are nonvanishing, and the numerical integration shows agreement with the exact analytic result¹⁴ to five places) the integrals converged to better than three places after four waves ($k=0, 1, 2, 3$). For $v=1$ convergence was obtained to better than three places after 5 waves, and for $v=2$ after 6 waves. For $v=.2$ the $k=1$ wave falls off by two orders of magnitude from the $k=0$ wave, and the $k=2$ falls off by three orders. For $v=1$ each wave after $k=0$ falls off by one order. Convergence was much slower for $v=2$, with waves after $k=0$ falling off by about $\frac{1}{2}$. For $v=4$ the integral peaked out at $k=1$ and gradually fell off. Except for $R=1.0$ the $v=2$ results are good to better than two places, and the $v=4$ results are good to only about one place. All other finite velocity results are good to better than three places.

The Heitler-London interaction at zero velocity is given by,

$$\frac{H_0(R) \pm H_1(R)}{1 \pm S(R)} \quad (3)$$

where,

$$H_0(R) = \langle 1s(1A) | 1s(2B) | (R^{-1} - r_{1B}^{-1} - r_{2A}^{-1} + r_{12}^{-1}) | 1s(1A) | 1s(2B) \rangle \quad (4)$$

At nonzero velocity it is given by,

$$\frac{H_0(R) \pm H_1(R, v)}{1 \pm S(R, v)} \quad (5)$$

$H_0(R)$ has been recalculated by Flannery and Levy¹⁵ and is the first diagonal matrix element in the coupled state calculation of Flannery¹¹. In Fig. 1 $H_0(R)$ and $H_1(R, v)$ are plotted as functions of R for laboratory velocities, 0, .2, 1, 2, and 4. In Fig. 2 $H_0(R) + H_1(R, v)$ and $H_0(R) - H_1(R, v)$ singlet and triplet interactions respectively are plotted for the same values of v . The numerical values for the individual matrix elements are given in Tables 1-5.

Discussion of Results

The most important aspect about the curves in Fig. 1 is the fact that the velocity dependent phase factors do not effectively reduce H_1 until quite high laboratory velocities. The trend of the curves is what would be expected on physical grounds. Greater velocities permit greater penetration of

the atoms, reflected in the shifted minima to smaller R . At 100 kev ($v \approx 2$) the exchange interaction has no negative (attractive) character, except above $R = 2.5$, where it is small and negative and approaches the axis from below. At 400 kev ($v = 4$) exchange is negligible. Fig. 2 shows the interesting result that at $v = 1$ and below the exchange forces show the familiar attractive Singlet well and the repulsive Triplet curve, whereas at $v = 2$ the Triplet curve is now attractive and the Singlet repulsive, suggesting the possibility of an oscillatory structure of the cross-section versus energy, observed in proton-helium direct excitation cross-sections¹⁶ to the higher excited 1P and 1D states and interpretable in the light of the above possibility as competing Singlet-Triplet scattering from the virtual charge transfer channel. Also of interest is the crossing of the $T(v = 1)$ and $S(v = 1)$ curve at about $R = 2.4$. Calculation of the excited state matrix elements for $H-H$ and the charge transfer matrix elements for H^+-He and the excitation cross-sections for these systems will answer this question and will be the subjects of later papers. It is clear from this study that electron exchange, long understood as the force which binds the hydrogen molecule and known to be important in low energy scattering, is also important in atomic collisions in which the nuclei and the bound electrons have comparable velocities.

Acknowledgement. The author wishes to thank Drs. F. H. M. Faisal and Felix T. Smith for interesting discussion, Dr. M. Riley for the use of his integrator, Difsys, Dr. A. Temkin for discussion of important mathematical points, and Mr. A. Silver for the subroutines to calculate the regular and irregular Legendre functions and the spherical Bessel function and for able computing assistance.

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12. Reference 10, p. 52.
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13. Reference 10, p. 266.

Table 1.

| $v = 0$ | | | | |
|---------|----------|-------------------------------|--------------|-----------------------------------|
| R | $H_0(R)$ | $\langle r_{12}^{-1} \rangle$ | $s^2 R^{-1}$ | $2S \langle r^{-1} \rangle$ |
| | | | | $\underline{\text{Sum}} = H_1(R)$ |
| .5 | .81245 | .567589 | 1.84451 | -1.74743 |
| 1.5 | -.0104 | .296835 | .350581 | -.809016 |
| 2.5 | -.0127 | .106622 | .084004 | -.263312 |
| 4.0 | -.00165 | .015627 | .008946 | -.034652 |
| | | | | .664669 |
| | | | | -.161600 |
| | | | | -.072686 |
| | | | | -.010079 |

Table II.

| $v = .2$ | | | | |
|----------|-------------------------------|--------------|-----------------------------|--------------------------|
| R | $\langle r_{12}^{-1} \rangle$ | $s^2 R^{-1}$ | $-2S\langle r^{-1} \rangle$ | $\text{Sum} = H_1(R, v)$ |
| .5 | .554125 | 1.77053 | -1.69343 | .631225 |
| 1.0 | .425346 | .705041 | -1.21927 | -.088883 |
| 1.5 | .288200 | .333837 | - .776388 | -.154351 |
| 2.0 | .177156 | .162715 | - .453547 | -.113676 |
| 2.5 | .102585 | .078895 | - .248533 | -.067053 |
| 3.0 | .05540 | .037678 | - .129620 | -.036542 |
| 4.0 | .014759 | .008149 | - .031548 | -.008640 |

Table III.

| $v = 1$ | | | | |
|-----------------|-------------------------------|--------------|-----------------------------|---------------------------------------|
| \underline{R} | $\langle r_{12}^{-1} \rangle$ | $S^2 R^{-1}$ | $-2S\langle r^{-1} \rangle$ | $\underline{\text{Sum}} = H_1(R_1 v)$ |
| .5 | .336378 | .733626 | -.860305 | .209699 |
| 1.0 | .246276 | .269844 | -.561502 | -.045391 |
| 1.5 | .155722 | .112911 | -.307796 | -.039163 |
| 2.0 | .088346 | .046672 | -.147059 | -.012041 |
| 2.5 | .046179 | .018418 | -.062372 | .002225 |
| 4.0 | .004472 | .000774 | -.002290 | .002956 |

Table IV.

| $v = 2$ | | | | |
|---------|-------------------------------|--------------|-----------------------------|--------------------------------------|
| R | $\langle r_{12}^{-1} \rangle$ | $S^2 R^{-1}$ | $-2S\langle r^{-1} \rangle$ | $\underline{\text{Sum}} = H_1(R, v)$ |
| .2 | .141447 | .302010 | -.237183 | .206274 |
| .5 | .124750 | .101400 | -.185327 | .040823 |
| 1.0 | .084355 | .027906 | -.084913 | .027348 |
| 1.5 | .04411 | .007083 | -.024547 | .02664 |
| 2.0 | .024515 | .001312 | -.003417 | .022410 |
| 2.5 | .008942 | .000122 | .000290 | .009354 |
| 4.0 | .00003 | .000012 | -.000179 | -.00014 |

Table V.

| $v = 4$ | | | | |
|---------|-------------------------------|--------------|------------------------------|--------------------------------------|
| R | $\langle r_{12}^{-1} \rangle$ | $s^2 R^{-1}$ | $-2s \langle r^{-1} \rangle$ | $\underline{\text{Sum}} = H_1(R, v)$ |
| .2 | .029200 | .007155 | -.013822 | .022533 |
| .5 | .020669 | .001568 | -.006528 | .015709 |
| 1.5 | .00144 | .000022 | -.00474 | -.00328 |

Figure Captions

Figure 1. $H_0(R)$ and $H_1(R,v)$ versus internuclear distance (atomic units). H_1 curves are labelled for laboratory velocities, 0, .2, 1, 2, and 4.

Figure 2. T (Triplet) and S (Singlet) resultant curves versus internuclear distance for the laboratory velocities indicated. The small hump in the $T(v=0)$ and $T(v=.2)$ are the result of the drawing.

