

*(e, 2e)* Probe for Hydrogen-Molecule Wave Functions\*

S. Dey, I. E. McCarthy, P. J. O. Teubner, and E. Weigold

*School of Physical Sciences, Flinders University of South Australia, Bedford Park, South Australia 5042, Australia*

(Received 18 November 1974)

The *(e, 2e)* reaction promises to be an extremely sensitive probe for molecular wave functions. As an initial test we have applied it to the H<sub>2</sub> and D<sub>2</sub> molecules in order to investigate its sensitivity to electronic and vibrational details. A detailed configuration-interaction wave function fits the data, whereas simpler functions do not. The simple Born-Oppenheimer approximation is confirmed to the accuracy of the experiment. The probe is compared with the Compton profile as a means of investigating the electron momentum distribution in H<sub>2</sub>.

The *(e, 2e)* experiment<sup>1</sup> has been developed as a probe for electron wave functions in atoms and molecules and their ions. For the helium atom we have shown by observing the angular correlation for excited-ion eigenstates that it is a fine enough probe to distinguish between Hartree-Fock and configuration-interaction wave functions.<sup>2</sup> The technique gives a very accurate description of the target-ion overlap function for resolved electronic states of the ion. A useful idea in a single-configuration model is that it measures the electron momentum distribution in the target.

A number of experimental techniques may be used to obtain information about electron momentum distributions in molecules. When thermal positrons annihilate in matter, the angular correlation between the decay photons is determined by the initial momentum distribution of the electrons. Unfortunately, the need to have accurate positron wave functions makes it difficult to obtain reliable momentum distributions by this method. The remaining two techniques are the *(e, 2e)* reaction and Compton scattering,<sup>3</sup> the latter including high-energy electron scattering.<sup>4</sup> These two techniques differ in several important ways. Whereas in the *(e, 2e)* technique the momentum distributions can be obtained directly for electrons in individual orbitals, the measurement of Compton profiles involves both summing over individual orbitals as well as integration over the momentum distributions.

For the simplest diatomic molecule, H<sub>2</sub>, the Compton-profile measurement does not involve summing over a number of orbitals, since both of the electrons in H<sub>2</sub> are in the same orbital. Hence it should be possible to compare directly the results of Compton and *(e, 2e)* measurements on H<sub>2</sub>. Furthermore, since H<sub>2</sub> is such a simple

molecule it should be possible to obtain good agreement between the calculated and measured momentum distributions. It is therefore quite disturbing to find that the photon<sup>3</sup> and electron<sup>4</sup> Compton profiles, as well as an early *(e, 2e)* measurement,<sup>5</sup> are all in disagreement with the results of theoretical calculations.

Although both photon and electron Compton profiles differ from the most accurate available theoretical profiles by only about 2%, this implies that the corresponding electron momentum distributions may be in disagreement by as much as 6% near  $q=0$ .

The simple impulse approximation, used in analyzing Compton profiles, gives a simple relation between the Compton profile  $J(q)$  and the electron momentum distribution  $\rho(q)$ , namely

$$\rho(q) \propto -q^{-1} dJ(q)/dq. \quad (1)$$

This relation may not be completely satisfied in the published experiments.<sup>3,6</sup> The *(e, 2e)* technique, on the other hand, measures  $\rho(q)$  directly without making the simple impulse approximation. It therefore offers an independent test of the theory.

The present accuracy of the *(e, 2e)* method is 5% in  $\rho(q)$  for small  $q$ , compared to a claimed accuracy of better than 1% in  $J(q)$  for the Compton profile. Since  $\rho(q)$ , for small  $q$ , is 3–4 times more sensitive to the actual shape of  $\rho(q)$  than is  $J(q)$ , the *(e, 2e)* method is comparable to the Compton method, even with reduced accuracy, in sensitivity to the shape of the momentum density.

The observed discrepancy between the theoretical and experimental momentum distributions could result from a failure of the Born-Oppenheimer approximation. Since the accuracy of this approximation depends on the nuclear mass being very much greater than the electron mass,

its breakdown is most likely to be observed in the light  $H_2$  molecule. For  $D_2$ , since the nuclei have twice the mass of the  $H_2$  nuclei, the Born-Oppenheimer approximation should be significantly better. In the present work we report detailed and accurate measurements of the  $(e, 2e)$  angular correlations for both  $H_2$  and  $D_2$  in order to test this hypothesis.

The present work was carried out using the noncoplanar symmetric geometry. In this geometry the energies of the two outgoing electrons in the ionizing collision are kept equal, their sum being equal to the total energy  $E$ , and both are emitted at the same angle relative to the incident electron direction. The angular correlation between the emitted electrons is obtained by changing the azimuth of one of the electron detectors. Since the details of the experimental technique have been described fully previously,<sup>7</sup> a description will not be repeated here. The experimental apparatus itself has been improved by the use of two new electron spectrometers which will be described in detail in a forthcoming publication on

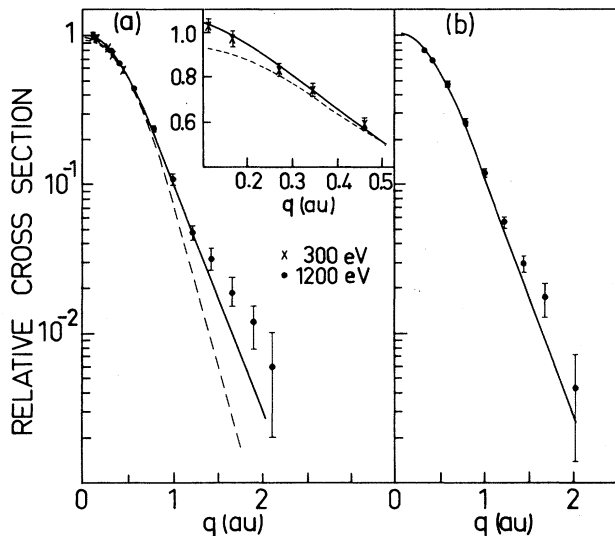


FIG. 1. Differential cross section for (a)  $H_2$  at  $E (=E_A + E_B)$  equal to 1200 and 300 eV, and (b)  $D_2$  at 1200 eV. The full curve in both figures is the theory of case 3 in the present work. Also shown in (a) are the cross sections calculated with the variational wave functions of Weinbaum (short-dashed line which continues into the full curve) and of Snyder and Basch (long-dashed line). Where no error bars (1 standard deviation) are shown, the errors are smaller than the dots. The inset in (a) shows details of the 300-eV experiment on  $H_2$  plotted on a linear scale. The full curve is the theory of case 3 and the dashed curve is calculated with the wave function of Weinbaum.

CO and  $N_2$ . The angular correlations obtained at total energies  $E$  of 300, 400, 600, and 1200 eV for  $H_2$  and  $D_2$  are shown in Figs. 1 and 2. They are plotted as a function of momentum transfer  $q$ , where  $\vec{q} = \vec{k}_0 - \vec{k}_A - \vec{k}_B$  and  $\vec{k}_0$ ,  $\vec{k}_A$ , and  $\vec{k}_B$  refer to the incident and final electron momenta, respectively, with  $k_A = k_B$ .

Statistical errors (shown by the error bars in the figures) range from 5% at small  $q$  to 60% at the largest values of  $q$ . Energy uncertainty is 4 eV, independent of energy. This enables closure over rotational and vibrational states to be used. Angles in each spectrometer are defined by a circular aperture of diameter  $4^\circ$ .

The basic theory of the  $(e, 2e)$  reaction,<sup>8</sup> which has been confirmed in extreme detail by applying it to atoms and, in particular, helium,<sup>2</sup> is the distorted-wave off-shell impulse approximation. Experience has shown that for atoms lighter than neon the plane-wave model is sufficient at 400-eV incident energy, with symmetric kinematics. For helium this is true at 200 eV. In the plane-wave approximation the  $(e, 2e)$  matrix element is

$$M = K t_C \langle r'v' | \langle \vec{k}_A, \vec{k}_B | \Psi_{\text{ion}} | \Psi_{\text{target}} \rangle | r v \rangle, \quad (2)$$

where  $K$  is a constant kinematic factor,  $t_C$  is the appropriate half-off-shell Coulomb  $t$ -matrix element, and  $|rv\rangle$  and  $|r'v'\rangle$  are initial and final rotation-vibration states, characterized by the appropriate sets of quantum numbers. The electronic wave functions for target and ion depend on the vibrational coordinates.

The full theory of this matrix element has been given by McCarthy.<sup>9</sup> In the present experiment, final rotation-vibration states are not resolved.

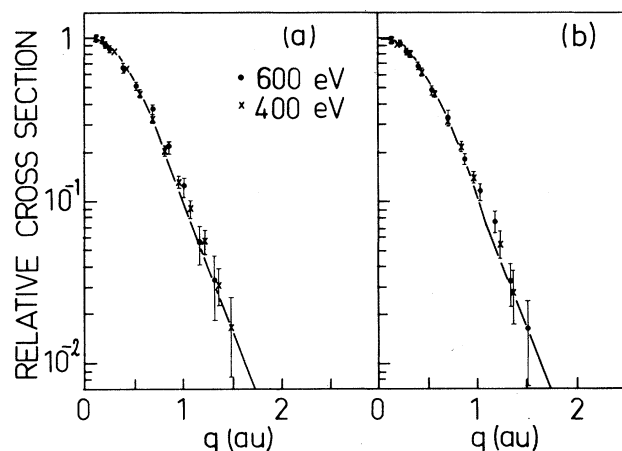


FIG. 2. Differential cross section for (a)  $H_2$  and (b)  $D_2$  at 600 and 400 eV. The curve is the theory of case 3 of the present work.

The initial vibrational state is the ground state. We assume that it is independent of rotational states.

The matrix element is written explicitly in terms of configuration-interaction functions for target and ion, using the abbreviation  $R$  to denote the set of nuclear coordinates  $\vec{r}_i$  for a general molecule,  $\vec{r}$  for the struck electron, and  $\rho$  for the electrons common to the target and the ion:

$$\begin{aligned}\Psi_{\text{target}} &= \sum_{\mu} f_{\mu}(R) \psi_{\mu}(\rho, R; \vec{r}), \\ \Psi_{\text{ion}} &= \sum_{\nu} g_{\nu}(R) \psi_{\nu}(\rho, R).\end{aligned}\quad (3)$$

The electronic overlap function depends only on  $\vec{r}$  and  $R$ . It may be expanded in a linear combination of atomic orbitals centered at the nuclei:

$$\langle \Psi_{\text{ion}} | \Psi_{\text{target}} \rangle = \sum_{\mu\nu} f_{\mu} g_{\nu} U(\vec{r}, R) \equiv \sum_{\mu\nu} f_{\mu} g_{\nu} \sum_{i_n} a_{i_n}^{(\mu\nu)}(R) u_{i_n}(\vec{r} - \vec{r}_i). \quad (4)$$

The plane-wave transform of this function is

$$\langle \vec{k}_A, \vec{k}_B | \langle \Psi_{\text{ion}} | \Psi_{\text{target}} \rangle | \vec{k}_0 \rangle \equiv \sum_{i_n} \varphi_{i_n}(\vec{q}, R) \exp(i\vec{q} \cdot \vec{r}_i). \quad (5)$$

The closure relation for final rotation-vibration states may be applied if such states are not resolved in the experiment.<sup>10</sup> This is

$$\sum_{r', v'} |r' v'\rangle \langle r' v'| = \delta(\vec{r}_1 - \vec{r}_1') \delta(\vec{r}_2 - \vec{r}_2') \dots \quad (6)$$

The expression for the differential cross section simplifies to the ground-state vibrational integral if we assume that rotational states are decoupled from the electronic and  $v=0$  vibrational states for  $H_2$ :

$$\sigma = K^2 t_C^2 \langle 0 | Q | 0 \rangle, \quad (7)$$

$$Q = C \left| \sum_n \varphi_{1n}(\vec{q}) \right|^2 [1 + j_0(qR)]. \quad (8)$$

Variational calculations of target and ion wave functions are available in the literature. Their parameters are given as functions of the vibrational coordinate  $R$ . We have tried three linear combinations of atomic orbitals as variational wave functions for the  $H_2$  molecule: Case 1, the function of Weinbaum,<sup>11</sup> which is a minimum-basis Slater wave function with a polarization term; Case 2, the function of Snyder and Basch,<sup>12</sup> where the atom-centered wave functions are linear combinations of several Gaussians computed only for the equilibrium value of  $R$ ; and Case 3, the configuration-interaction function of McLean, Weiss, and Yoshimine,<sup>13</sup> which obtains the correct binding energy within 4%. The second of these wave functions describes the  $H_2$  electronic function as a determinant of molecular orbitals. Hence the molecule-ion overlap is a product of a constant factor and one molecular orbital. Only in this approximation can we say that the experiment measures the momentum-space wave function of the molecule.

For functions 1 and 3 we require a variational wave function for the ion. For case 1, we used the simple function of Finkelstein and Horowitz.<sup>14</sup> For case 3 we used the wave function of Guillemin and Zener,<sup>15</sup> which obtains the correct binding energy within 0.05%.

In cases 1 and 2 no vibrational integral was performed. In case 3 the full vibrational integral was performed. It was found to give an angular correlation which could not be distinguished in shape from the square of the Fourier transform of the electronic overlap function, calculated at the equilibrium value of  $R$ . In all cases the theoretical calculation was averaged over finite acceptance angles of  $4^\circ$ .

Results are shown in Figs. 1 and 2. Case 3 fits the data in detail over approximately 2 orders of magnitude at all the energies tried. No difference is observed between  $D_2$  and  $H_2$ , either in the theory or in the data, thus confirming the Born-Oppenheimer approximation to the accuracy of this experiment.

The self-consistent field calculation of Snyder and Basch seriously underestimates the high-momentum (short-distance) components, but the simple Weinbaum theory is distinguishable from the data only for very small momentum transfers (large distances). Detail of this is shown in the inset of Fig. 1.

Since one overall multiplicative factor is not determined by the experiment, some conventional normalization must be used. For case 3, in which the theoretical and experimental shapes agree very well, the theory is normalized to fit the data for  $q$  less than 1 a.u. This normalization of course makes the effective number of

bound electrons equal in theory and experiment. The same practice is used for x-ray and  $\gamma$ -ray Compton-profile normalization but not in the high-energy electron-impact method. For the other two theories the theoretical curves have been arbitrarily placed on the logarithmic scale in the best way to emphasize shape discrepancies.

The discrepancy between theory and experiment in the earlier ( $e$ ,  $2e$ ) measurements<sup>5</sup> can be explained in part. Firstly, the theory used was slightly in error, since the sum over vibrational states was not carried out although these states were summed over in the experiment. Secondly, there was a systematic error of 6% in the calibration of  $q$ .

The small discrepancy between theory and experiment in the Compton-profile measurements gives rise to a more serious disagreement between the calculated and experimentally derived momentum distributions. This discrepancy could quite possibly be due to failure to satisfy binary-encounter conditions in the experiments. If this is indeed the case then, as in ( $e$ ,  $2e$ ), the measured Compton profiles will depend on the overlap of the initial target and final ion wave functions rather than the single-particle momentum densities. Of course at sufficiently high energy, closure over final states reduces the theory to dependence only on initial states.

We would like to acknowledge very helpful conversations with Dr. R. A. Bonham, Dr. W. A.

Reed, Dr. R. J. Weiss, and Dr. H. F. Wellenstein.

\*Work supported by the Australian Research Grants Committee.

<sup>1</sup>E. Weigold, S. T. Hood, and P. J. O. Teubner, Phys. Rev. Lett. **30**, 475 (1973).

<sup>2</sup>I. E. McCarthy, A. Ugbabe, E. Weigold, and P. J. O. Teubner, Phys. Rev. Lett. **33**, 459 (1974).

<sup>3</sup>P. Eisenberger, Phys. Rev. A **2**, 1678 (1970).

<sup>4</sup>R. A. Bonham and H. F. Wellenstein, Int. J. Quantum Chem., Symp. **1973**, 377.

<sup>5</sup>E. Weigold, S. T. Hood, I. E. McCarthy, and P. J. O. Teubner, Phys. Lett. **44A**, 531 (1973).

<sup>6</sup>R. C. Ulsh, R. A. Bonham, and L. S. Bartell, Chem. Phys. Lett. **13**, 6 (1972).

<sup>7</sup>E. Weigold, S. T. Hood, and I. E. McCarthy, Phys. Rev. A **11**, 566 (1975).

<sup>8</sup>S. T. Hood, I. E. McCarthy, P. J. O. Teubner, and E. Weigold, Phys. Rev. A **8**, 2494 (1973), and **9**, 260 (1974).

<sup>9</sup>I. E. McCarthy, J. Phys. B: Proc. Phys. Soc., London **6**, 2358 (1973).

<sup>10</sup>T. Iijima, R. A. Bonham, and T. Ando, J. Phys. Chem. **67**, 1472 (1963).

<sup>11</sup>S. Weinbaum, J. Chem. Phys. **1**, 593 (1933).

<sup>12</sup>L. C. Snyder and H. Basch, *Molecular Wave Functions and Properties* (Wiley, New York, 1972).

<sup>13</sup>A. D. McLean, A. Weiss, and M. Yoshimine, Rev. Mod. Phys. **32**, 211 (1960).

<sup>14</sup>B. N. Finkelstein and G. E. Horowitz, Z. Phys. **48**, 118 (1928).

<sup>15</sup>V. Guillemin, Jr., and C. Zener, Proc. Nat. Acad. Sci. U. S. **15**, 314 (1929).

## Effects of Time Ordering on Plasma-Broadened Hydrogen Profiles

Larry J. Roszman

*Institute for Basic Standards, National Bureau of Standards, Washington, D. C. 20234*

(Received 3 February 1975)

The plasma-broadened  $H_\alpha$  and  $H_\beta$  spectral-line profiles of hydrogen were calculated retaining the time ordering in the  $S$  matrices of the width-shift operator by diagonalizing with the  $O(4)$  group. Significant changes occur: The  $H_\alpha$  peak is decreased 15%, the half-width is increased 25%, and the  $H_\beta$  relative dip is decreased 23% without significant alteration of the maximum intensity of half-width. Agreement with experiment is improved appreciably.

The plasma- (Stark-) broadened Balmer-line profiles of hydrogen measured during recent experiments<sup>1,2</sup> exhibit much less structure in their central regions than predicted by the most comprehensive theories.<sup>3-7</sup> This difference is quite serious since the plasma-broadened Balmer lines have found many applications as a convenient pre-

cision diagnostic tool for determination of charged-particle densities in plasmas. Preliminary examinations of the several approximations which might significantly affect the central structure—neglect of time ordering,<sup>8-13</sup> ion motion,<sup>2, 14-17</sup> and inelastic collisions<sup>18, 19</sup>—indicate that the neglect of time ordering in calculations of the ma-