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High-energy electron scattering study of molecular hydrogen

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Energy-resolved electron scattering from H_2 was measured using high-energy electrons. The 40-kV energy-unresolved data of Ketkar and Fink [Phys. Rev. Lett. **45**, 1551 (1980)] were reanalyzed and combined with our 30-keV elastic measurements to calculate the inelastic cross section. Although the angular dependence of the cross section shows good agreement with recent quantum calculations over a large part of the angular region, some discrepancies remain at $s \approx 4$ a.u. in the elastic and inelastic cross section and around $s \approx 2$ a.u. in the total cross section. The elastic cross section at very small angles is compared with theoretical predictions and values derived from the magnetic susceptibility.

Because of its simplicity, many properties of the molecular wave function of the hydrogen molecule have been studied extensively. Since the hydrogen atom only has one electron, correlation effects in the molecule exist only in the binding. Very accurate molecular wave functions are available today and cross sections of x-ray and electron scattering have been calculated in the first Born approximation invoking closure arguments. Many scientists have contributed to this discipline. Liu and Smith[1] calculated elastic, inelastic, and total (elastic plus inelastic, referred to as the energy-unresolved) differential cross sections using the self-consistent-field (SCF) and configuration-interaction (CI) wave functions of Davidson and Jones, which included 96% of the correlation energy. More recent calculations have been carried out by Kołos, Monkhorst, and Szalewicz[2] using a correlated Gaussian wave function (CGF). Their calculations not only achieved 99.9% of the correlation energy, but also took into account the vibrational and rotational motions of the molecule in the case of energy-unresolved scattering.

Previous electron scattering data from H_2 were for total scattering[3-6] and showed discrepancies with theoretical calculations for the scattering of 40-keV electrons. An oscillatory behavior existed in the difference function between the measured scattering intensity and that calculated from the independent-atom model[7] (IAM), particularly at large angles. This behavior was indicated by a calculation of Liu and Bonham,[8] who used a rather coarse approximation to account for the average due to the vibrational motion. However, more recent calculations by Kołos, Monkhorst, and Szalewicz[2] did not confirm this trend. Doubts have remained since this discrepancy was found. We have reanalyzed the raw data of Ketkar and Fink using new atomic scattering factors and the results are presented below together with 29.4-keV elastic scattering cross sections recently measured.

The experimental arrangement used to measure elastic scattering has been described in detail elsewhere.[9,10] In this measurement, a 29.4-keV electron beam is crossed with the target gas beam at 90° and the scattered electrons are energy analyzed using a Möllenstedt analyzer.[11,12] Electrons that are inelastically scattered, that is, those which transfer energy to the electronic internal degrees of freedom of the molecule, are rejected by the analyzer. Note that because of the finite resolution of the analyzer, the definition of inelastic scattering in the experiment does not include pure vibrational and rotational transitions. The scattered intensity as a function of the angle is measured by rotating the electron beam in the scattering plane.

One of the major differences between this experiment and the previous ones performed on the same equipment is the improvement in background subtraction. In the older experiments, two separate measurements were taken, one with gas flowing from the main nozzle at the center of rotation, the other with gas flowing through a different nozzle attached to the side of the vacuum chamber. The chamber pressure was maintained at the same level for the two measurements. This method did not automatically lead to the correct result since the pressure distributions in the chamber were not identical for the two conditions. Usually this difference can be neglected for heavier molecules, since the scattering intensity is proportional to Z^2, where Z is the atomic number of the scattering target. But in the case of hydrogen, the scattering intensity is so much smaller than for all previously measured samples that background scattering from impurities in the vacuum chamber becomes relatively large.

Another contribution to the background comes from the residual gas scattering. Since the pumping speed of the vacuum pumps for lighter molecules is larger than for heavier molecules, H_2 scattering has to compete with a higher percentage of residual gas than other targets. Because the correction of these two errors is so critically important in this experiment, the pressure distributions of the two measurements have to be made almost identical to get the most accurate background subtraction. A movable nozzle consisting of a hypodermic needle mounted on a block which can be moved in the X, Y, and Z directions from outside the chamber was used for this purpose. The nozzle is initially set at the center of rotation so that the gas beam crosses the electron beam during a main beam measurement. The nozzle is then moved off center where it misses the electron beam by about 2.5 mm for a measurement of the residual gas contribution to the scattering.

In order to assure high-purity hydrogen gas, a palladium filter was used. Since hydrogen has a high diffusion coefficient in palladium, it will pass through the filter when the palladium is heated. This method is very effective in removing water and organic impurities, enabling us to have a purity of better than 99.999%. The filtered gas flows through an electronically controlled pressure regulator and is eventually sent to the nozzle of the experiment. The gas-feeding system is shown in Fig. 1.

To obtain the absolute cross section, the measured intensity is first corrected for misalignment due to the detector being positioned a small amount out of the scattering plane and then matched to the IAM scattering at large angles whee the scattering behavior is assumed to be dominated by the nuclear potential. The Fourier transform of the cross section is used to determine the bond length and the precise energy of the electron beam.[13] This analysis was performed on both the present elastic scattering data and the energy-unresolved results of Ketkar and Fink. The parameters obtained from the analysis are listed in Table I.

Because the data are measured as a function of the scattering angle θ rather than as a function of the momentum transfer s, several corrections must be applied to the inelastic part of the data to account for the change in the center of mass for ionizing collisions, the change in the acceptance cone of the detector as a function of the scattering angle, and the exchange of electrons in the scattering process.[14] Since these effects are small, and since we are unable to make corrections to the theoretical curves, we corrected the experimental data by changing our independent-atom model and assuming that the effects would be subtracted away when calculating $\Delta\sigma$. The exchange effect was found to be negligible in the elastic data, but noticeable in the total and inelastic data.

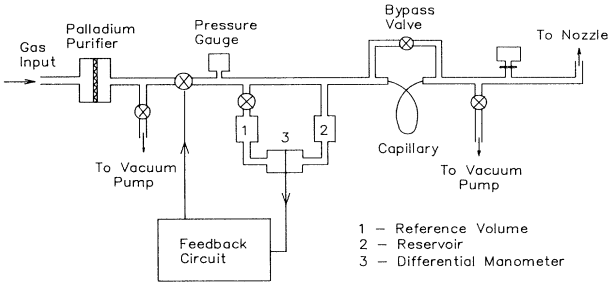

FIG. 1. Gas-feeding system of the experiment. (a) Hydrogen gas flows through a palladium filter and is pressure regulated and sent to the movable nozzle. (b) Gas pressure regulator of the experiment. A constant pressure is kept in the reference volume (1). The difference of pressure between the reservoir (2) and the reference volume is detected by a differential manometer (3) and the signal is sent to a feedback circuit to control a PV-10 piezoelectric valve. A capillary tube is used to further stabilize the pushing pressure.

TABLE I. Parameters derived from data analysis.

	R_e (Å)	R_g (Å)	l_e (Å)	Energy (eV)
Elastic work	0.7414(15)	0.7537(14)	0.0849(17)	29 350±5
Total work	0.7418(9)	0.7542(9)	0.0849(7)	42080±5

The elastic scattering results of the present experiment are shown in Fig. 2. The difference function[7] $\Delta\sigma$ is defined as a quantity proportional to s^4 times the difference of the scattering cross section obtained from the measurement and from the IAM, where s is the momentum transfer $[s=4\pi/\lambda\sin(\theta/2)]$, λ is the wavelength of the incoming electrons, and θ is the scattering angle. $\Delta\sigma$ is given in atomic units by

$$\Delta\sigma(s)=\frac{s^4}{4\gamma^2}(I_{\text{expt}}-I_{\text{IAM}}) ,$$

where γ^2 is the relativistic correction. Since there is no atomic correlation in hydrogen, this difference function reveals molecular binding including correlation effects. Tavard's theorem[15] states that the integrals of the $\Delta\sigma$ curves are related to the Coulombic, pair correlation, and exchange interactions of the bond electrons. These properties will be discussed below for the elastic, total, and inelastic difference functions, respectively.

The present experimental data are compared with several calculated results. Note that the elastic difference function presented here is not oscillatory at large momentum transfers. Liu and Smith's[1] (referred to as LS) CI elastic difference functions, as well as the calculations by Kołos, Monkhorst, and Szalewicz[2] (referred to as KMS),

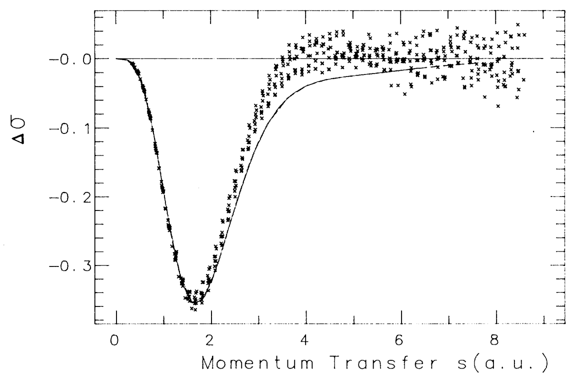

FIG. 2. Elastic difference function of 29.4-keV elastic scattering. Crosses, this work; solid line, calculation of LS; dashed line, quasielastic result of KMS with clamped nuclei.

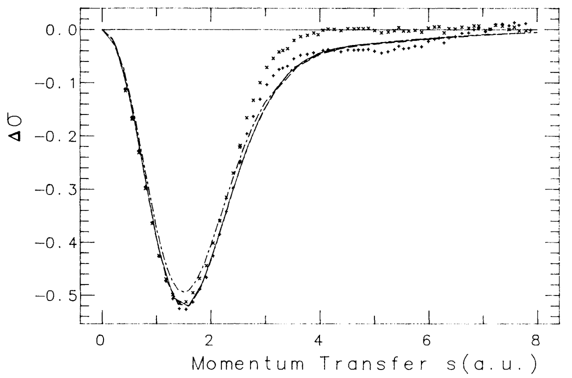

FIG. 3. Total difference functions. Crosses, Ketkar and Fink's 40-keV data reanalyzed. Pluses, Ketkar and Fink's data with the corrections of Ref. 14 applied. Solid line, calculation by LS; dashed line, KMS result using clamped nuclei; dot-dashed line, KMS averaged over the rotational and vibrational motion.

are shown in Fig. 2 for comparison. The dashed line is KMS's calculation using a ground-state wave function with clamped nuclei ($R=1.4009$ a.u.), but which accounts for the occupation of the rotational states by a Boltzmann distribution and all possible transitions to other rotational states by the scattering electrons. Since no vibrational effects have been considered, the dependence of the rotational states on the vibrational states has been ignored. Thus, at this time vibrational effects have not been included in the calculation of the quasielastic cross section. The results of Liu and Smith, who also did not take vibration of the molecule into account, are given by the solid line and are essentially indistinguishable from KMS. Our experiment agrees well with the theoretical results for $s<2$ a.u., but for large s the theory remains below the data. This is not unexpected since the effect of the zero-point vibration is not included in the calculation.

The reanalyzed total data are presented in Fig. 3. Again, a difference between the experiment and all of the theories is found. As will be discussed later, this will also lead to differences in the integrals of the $\Delta\sigma$ curves which are related to the dissociation energies. The effect of the scattering cone, exchange, and center-of-mass corrections of Ref. 14 can also be seen in the picture. Since the tail of the corrected curve for $s>5$ a.u. is no longer flat, it is no longer valid to scale to data by matching it to the independent-atom model in this region. However, when the data are instead scaled to one of the theories (KMS, for example), fairly good agreement is obtained.

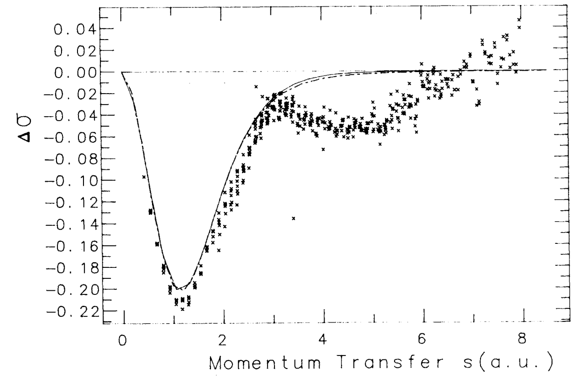

FIG. 4. Inelastic difference function obtained by subtracting the elastic data curve from the total difference function. Crosses, derived from experiments; solid line, LS result; dot-dashed line, quasi-inelastic result of KMS with clamped nuclei.

TABLE II. Interaction energies derived from the integrals of the $\Delta\sigma$ curves.

ΔV (eV)	$\Delta V_{n\text{-}e}+\Delta V_{e\text{-}e}$ (Coulomb (eV)	$\Delta V_{e\text{-}e}$ (exchange) (eV)
-4.6 ± 0.2	-2.4 ± 0.2	-1.6 ± 0.2

There are several experimental and theoretical possibilities for the origin of the discrepancies. Experimentally, one can never rule out small impurities in the gas sample. The $\Delta\sigma$ curves show that the impurities cannot be molecular, but rare gasses cannot be excluded. While it is unlikely that the two experiments (total and elastic data) have the same concentrations of atomic impurities, one cannot conclusively eliminate this possibility. Misalignment of the two apparatuses is also unlikely since both data sets were accumulated in two different apparatuses more than nine years apart.

The theory used could be the source of the discrepancy since the theoretical $\Delta\sigma$ curve is based on a bond length of 1.4009 a.u. while the experimental value is 1.4018 a.u. This is only a small difference, but previous calculations showed a strong sensitivity of the $\Delta\sigma$ curve to the molecular structure parameters. Another possibility for the discrepancy is the validity of the closure procedure. For the evaluation of the inelastic scattering cross section, the closure procedure is used so that the calculations can be based exclusively on the ground-state wave function of the molecule. This is not essential for vibrational or rotational averaging since the reduced mass makes these contributions exceedingly small. However, the electronically excited states deserve further consideration.

The inelastic difference function is derived from the

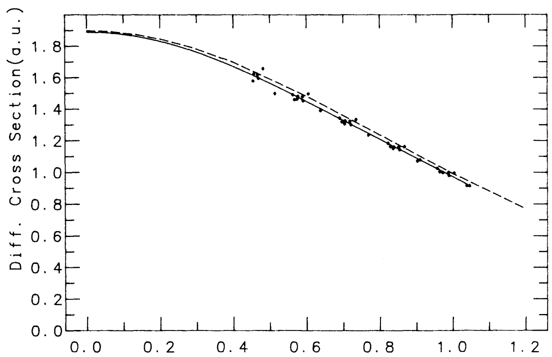

FIG. 5. The elastic differential cross sections at very small angles. Crosses, this work; solid line, least-squares-fitted curve; dashed line, KMS.

TABLE III. Small-angle scattering and charge-density properties (in atomic units unless otherwise indicated).

	$A=(\frac{d\sigma}{d\Omega})_{\theta=0}/\gamma^2$	B	C	$\langle r^2\rangle^{\mathrm{d}}$	$\langle z^2\rangle^{\mathrm{f}}$	χ^{d} ($10^6\mathrm{cm}^3/\mathrm{mol}$)[g]
This work	1.89±0.08	−1.5±0.1	0.9±1.7	5.1±0.1[e]	2.1±0.1	−4.0±0.1
SCF-DJ[a]	1.9530	−1.404	0.641 84	5.169	2.221	−4.093
Ci-DJ[a]	1.8989	−1.3472	0.606 72	5.111	2.211	−4.048
KW[b]	1.8992			5.094	2.046	−4.034
Expt.[c]				5.189	2.041	−4.1097

[a] DJ denotes E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962).

[b] KW denotes W. Kołos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965). These values apply to $R=1.40a$.

[c] Values from Table V of Ref. 17.

[d] $\langle r^2\rangle = Z\langle R_e^2\rangle_{\mathrm{vib}}/2-\left[9\left[\frac{d\sigma(0)}{d\Omega}\right]_{\mathrm{el}}/\gamma^2a_0^2-\frac{4}{5}\langle Q\rangle_{\mathrm{vib}}^2\right]^{1/2}$.

[e] We used the quadrupole moment calculated by Kołos and Wolnewicz (footnote b above) ($Q_2=0.6155$ esu cm^2$=0.4576$ a.u.).

[f] $\langle z^2\rangle=\frac{1}{3}(\langle r^2\rangle+2Q_e)$, $Q_e=-\langle Q\rangle_{\mathrm{vib}}$.

[g] $\chi^d=-0.791\,93\times10^{-6}[\langle r^2\rangle(\mathrm{a.u.})]\mathrm{cm}^3/\mathrm{mol}$. χ^d is the diamagnetic susceptibility.

elastic and the total data. The assumption was made that the difference functions are energy independent, which is justified in the range of validity of the first Born approximation. A study of this was carried out by Fink, Moore, and Gregory[16] for the scattering of N_2. Shown in Fig. 4 is the inelastic difference function obtained by subtracting the spline interpolation of the elastic difference function from the total difference function. Our experimental results agree well with LS for $s<3$ a.u., but a discrepancy is found at $s\approx5$ a.u. Again this is not surprising since the vibrational motion of the molecule was not included in this calculation and a correction to the closure assumption needs to be made.

Using the integrals of the difference functions, various interaction energies can be studied. The following relations are used:[7,8]

$$\Delta V_{n\text{-}n}+\Delta V_{n\text{-}e}+\Delta V_{e\text{-}e}=\frac{1}{\pi}\int ds\,\Delta\sigma_{\mathrm{tot}}(s)\ ,$$

$$\Delta V_{n\text{-}n}+\Delta V_{n\text{-}e}+\Delta V_{e\text{-}e}(\mathrm{Coulomb})=\frac{1}{\pi}\int ds\,\Delta\sigma_{\mathrm{el}}(s)\ ,$$

$$\Delta V_{e\text{-}e}(\text{non-Coul.})=\Delta V_{e\text{-}e}(\text{exchange})=\frac{1}{\pi}\int ds\,\Delta\sigma_{\mathrm{inel}}(s)\ ,$$

where the indices *n-n*, *n-e*, and *e-e* correspond to the nucleus-nucleus, nucleus-electron, and electron-electron interactions and the *e-e* interaction is composed of a direct Coulomb and an exchange part. Integration of the inelastic $\Delta\sigma$ curve gives the exchange interaction energy directly since the IAM does not have this term. The evaluated energies are listed in Table II. The dissociation energy can be determined by adding ΔV determined from the data curve to the dissociation energy E_m of the IAM. The binding energy of the IAM can be calculated by integrating the molecular interference function $s^4M(s)$.[7] Evaluation of this integral led to $E_m=0.016$ eV, which does not agree with the calculation by Kołos, Monkhorst, and Szalewicz[2] ($E_m=0.032$ eV). However, the values resulting from both evaluations are less than the precision of this experiment. The dissociation energy obtained from the total data which has not been corrected for exchange is 4.0±0.2 eV and the value obtained from the corrected data is 4.6±0.2 eV. These values are close to but not exactly equal to the spectroscopic value of 4.49 eV. The origin of this discrepancy may again be the failure of the closure approximation for the electronic excited states.

Forward elastic scattering is of interest because it is related to the molecular moments and other properties.[17,18] Normally the elastic differential cross section of homonuclear diatomic molecules can be expanded as a function of the momentum transfer,

$$\frac{d\sigma_{\mathrm{el}}(s)}{d\Omega}\bigg/\gamma^2=A+Bs^2+Cs^4+\cdots\ ,$$

where the coefficients A, B, and C are related to the multipole moments and diamagnetic susceptibility. Liu[18] carried out calculations of these coefficients using various wave functions. Also, a least-squares fit to the elastic data was made to determine these coefficients experimentally. The data are plotted in Fig. 5 and compared with the KMS result, which agrees with the measured data within the experimental uncertainty. The coefficients and several other properties derived using the formulas given in Ref. 17 are listed in Table III. The derived quantities agree well with the magnetic susceptibility and other *ab initio* calculations.

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