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Determination of the electronic structure of atoms and molecules in the ground state: Measurement of molecular hydrogen by high-resolution x-ray scattering

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The high-resolution x-ray-scattering technique is used to study the elastic scattering of atoms and molecules in the gas phase. The elastic squared form factor, which is the square of the Fourier transformation of the electron density distribution in position space and reveals the pure electronic structure of atoms and molecules in the ground state, of molecular hydrogen is measured at an incident photon energy of about 9889 eV and an energy resolution of about 70 meV. Although it is generally thought that the x-ray-scattering technique is identical to high-energy electron scattering, at least for elastic scattering these two techniques have an apparent difference, i.e., the pure electronic structure of a molecule in the ground state can be determined by x-ray scattering while it cannot be obtained by the high-energy electron impact method due to the interference between the scattering of separate nuclei and of the electrons in the target. The present experimental results match the theoretical calculations very well, which demonstrates that high-resolution x-ray scattering is a powerful tool to study the electronic structure of atoms and molecules in the ground state.

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The x-ray-scattering technique is a common experimental method used to measure and analyze the property and structure of materials, such as in crystal structure analysis [1], the determination of protein structures [2], structure-based drug design [3], etc. In these applications, the physical basis is the elastic scattering of the x ray by atoms or molecules in the target, e.g., the x-ray diffraction pattern of a crystal is a function of the structure factor in which the elastic form factor of atoms or molecules is a key parameter [4]. Therefore, the elastic scattering cross sections of an x ray by atoms and molecules play a crucially important role in the development of these fields. Although the x-ray-scattering technique has served as a method to measure and analyze the material structure over a whole century since Bragg diffraction was found in 1912, here we discuss a high-resolution measurement of the elastic differential cross section of x-ray scattering for gas-phase atoms and molecules (the simplest diatomic molecule of hydrogen). Currently, all the data used in x-ray diffraction structure analysis come from theoretical calculations [4], which should be tested stringently by experiment. Therefore, the high-precision measurement of the differential cross section of x-ray elastic scattering of atoms and molecules is very important and meaningful. This is what we want to do in this Brief Report.

The main reason for the shortage of experimental cross sections of x-ray elastic scattering of atoms or molecules is the extremely low cross section, which is proportional to r_0^2, where r_0 is the classical electron radius. Although several experiments have been carried out to measure the differential cross section of x-ray elastic scattering of noble gases [5–7], the detectors used in these works, i.e., the intrinsic Ge planar detector [5,6] and the scintillation counter [7], have an energy resolution of only about several hundred eV, which may resolve the elastic scattering and the Compton scattering at large scattering angles, but they cannot resolve the elastic scattering and inelastic excitations because the excitation energy of the valence shell transition of atoms and molecules is less than 25 eV, which is much less than the energy resolution of these detectors. Furthermore, the ionization continuum also contributes to the elastic scattering in these experiments due to the same reason. So these previous elastic differential cross sections definitely have contributions from the inelastic scattering, which have been observed recently by inelastic x-ray-scattering experiments [8–11]. Because of the lack of experimental data, only Bentley *et al.* [12,13] have calculated the elastic squared form factor of molecular hydrogen using ground wave functions prepared by different theoretical methods [14]. With the dramatic development of third-generation synchrotron radiation and the crystal spectrometer, the brightness and the energy resolution of the x-ray-scattering technique have been greatly improved, which provides the possibility for high-precision measurements of the elastic differential cross section of x-ray scattering by atoms and molecules. Recently, the dynamic parameters of the valence shell excitations of some atoms and molecules have been measured by the x-ray-scattering technique with high-energy resolution in our group [8–11] and with moderate-energy resolution in Seidler's group [15,16], and some interesting excitation mechanisms have been revealed. In this Brief Report, we extend this experimental technique to study the elastic scattering of the x ray by a free molecule, and pure electronic structure information about the ground state is determined.

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According to the definition, the elastic squared form factor $\zeta(\mathbf{q})$ can be written [4,17,18] as

$$\zeta(\mathbf{q}) = \left| \langle \Psi_0 | \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j} | \Psi_0 \rangle \right|^2 = \frac{1}{r_0^2} \frac{1}{|\varepsilon_i \cdot \varepsilon_f^*|^2} \left(\frac{d\sigma}{d\Omega} \right)_\gamma . \quad (1)$$

Here $\mathbf{q}$ is the vector of the momentum transfer, while Ψ_0 stands for the ground-state wave function of the target. ε_i and ε_f stand for the polarization directions of the incident and scattered photons, respectively. The sum is over all electrons and $\mathbf{r}_j$ is the position vector of the jth electron. $(\frac{d\sigma}{d\Omega})_\gamma$ is the elastic differential cross section of the x-ray scattering and is measured as a function of the scattering angle. It can be seen clearly that $\zeta(\mathbf{q})$ can be determined from the experimental differential cross sections measured by high-resolution x-ray elastic scattering.

For a diatomic molecule, the wave function of the ground state can be written as

$$\Psi_0 = \Psi_e(\mathbf{r},R)\Psi_v(R)\Psi_{JM}(\theta,\varphi). \quad (2)$$

Here $\Psi_e(\mathbf{r},R)$, $\Psi_v(R)$, and $\Psi_{JM}(\theta,\varphi)$ are the electronic, vibrational, and rotational wave functions, respectively, with θ and φ being the orientations of the molecular axis. $v = 0$ and J have a distribution because most experiments are carried out at room temperature. Then the elastic form factor can be written as [18]

$$\begin{aligned} &\varepsilon(\mathbf{q}; e,0,JM \leftarrow e,0,JM) \\ &\quad = \iiint Y_{JM}^*(\theta,\varphi)\Psi_0^*(R)\varepsilon_0(\mathbf{q}; R,\theta,\varphi)Y_{JM}(\theta,\varphi)\Psi_0(R) \\ &\quad \times dR \sin\theta d\theta d\varphi, \end{aligned} \quad (3)$$

with

$$\begin{aligned} \varepsilon_0(\mathbf{q}; R,\theta,\varphi) = \int \Psi_e^*(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,R) \sum_{j=1}^{N} e^{i\mathbf{q}\cdot\mathbf{r}_j} \\ \times \Psi_e(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N,R) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N \end{aligned}$$

being a part of the elastic form factor which is related to the electronic state. R is the internuclear distance, and JM stands for the rotational quantum numbers of the diatomic molecule.

Although $|\varepsilon(\mathbf{q}; e,0,JM \leftarrow e,0,JM)|^2$ gives the most accurate description for the elastic scattering of a diatomic molecule, most collision experiments cannot resolve the rotational transitions. So averaging the population of the rotational states and neglecting the weak dependence of $\varepsilon(\mathbf{q}; e,0,JM \leftarrow e,0,JM)$ on different J, the elastic squared form factor can be written as

$$\begin{aligned} \zeta(\mathbf{q}) &= |\varepsilon(\mathbf{q}; e,0 \leftarrow e,0)|^2 \\ &= \frac{1}{4\pi} \iint \sin\theta d\theta d\varphi \left| \int \Psi_0^*(R)\varepsilon_0(\mathbf{q}; R,\theta,\varphi)\Psi_0(R) dR \right|^2. \end{aligned} \quad (4)$$

Here the spherical averaging is due to random orientation of the diatomic molecule. Therefore, the calculated results from Eq. (4) can be compared with the experimental result.

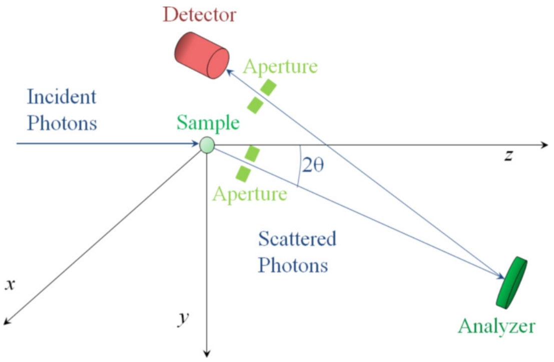

FIG. 1. (Color online) Schematic of the experimental setup for the high-resolution x-ray scattering of gases at the Taiwan Beamline BL12XU of SPring-8.

The present measurement was carried out at the Taiwan Beamline BL12XU of SPring-8 with an incident photon energy of about 9889 eV and an energy resolution of about 70 meV. The experimental setup used in this work is shown in Fig. 1 and has been described in our previous works [8–11]. Briefly, a Si(333) monochromator was used to achieve a high-energy resolution of 70 meV. Si(555) spherical analyzers with a 2-m radius of curvature were used to collect the scattered photons. In the measurement, the analyzer energy for the scattered photon was fixed at 9889.90 eV, while the incident photon energy was varied, by which the energy loss was deduced and the elastic peak was recorded. In the present experiment, two different sample gases (hydrogen and helium gases) with pressures of 8.94 and 6.88 atm were sealed in turn in a gas cell by a Kapton window, and then the gas cell was put on the experimental platform for the measurement in turn. The transmittances of hydrogen and helium were measured and both of them were 99.9%, so there was no need to correct the absorption by the gases of helium and hydrogen. In addition, the spectra with and without hydrogen gas were recorded, and the counts of the latter were deducted as the background. All the spectra of molecular hydrogen within the scattering angular range of 10°–70° for elastic scattering and atomic helium within the scattering angular range of 10°–18° for the $1s^2 \rightarrow 1s2p$ transition were taken at room temperature.

The gas cell used in this work had a diameter of 30 mm, so the long interaction length of 30 mm of the x ray and the target resulted in a variation of the collision length viewed by the analyzer, which was proportional to $1/\sin(2\theta)$ at larger scattering angles of $2\theta > 15^\circ$, which is a well-known result in the electron-atom/molecule scattering community [19,20]. Because of the limited size of the gas cell, the collision length at $2\theta \leq 15^\circ$ deviated from the rule of $1/\sin(2\theta)$ and was corrected by measuring the elastic scattering of hydrogen and of the excitation of $2\,^1P$ of helium since the $\zeta(\mathbf{q})$ of $2\,^1P$ of helium is well known, and has been measured and calculated with a high accuracy and has proven to be reliable [8,21–23]. In this way the variable collision lengths at 20°–70° of molecular hydrogen were simply calibrated by multiplying by a factor of $\sin(2\theta)$ while the ones at 10°–15° were calibrated by multiplying the intensity ratios of the elastic scattering of hydrogen to the $2\,^1P$ of helium with the $\zeta(\mathbf{q})$ of the $2\,^1P$ of helium [23]. Since the incident photon beam was linearly polarized and its direction was in the scattering plane, a factor of $\cos^2 2\theta$ was corrected according Eq. (1). Then the squared form factor $\zeta(\mathbf{q})$ for the elastic scattering

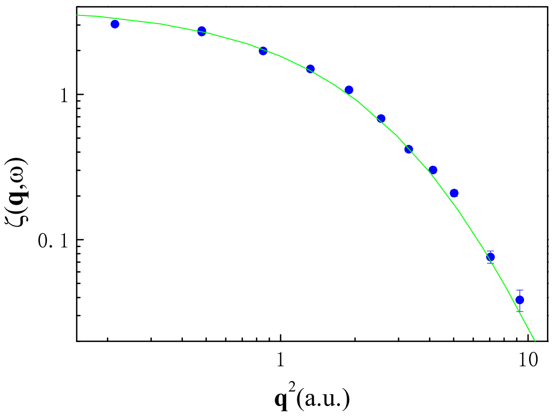

FIG. 2. (Color online) Elastic squared form factor $\zeta(\mathbf{q})$ of molecular hydrogen. Solid blue circle: Present x-ray-scattering results. Green solid line: The theoretical results of Bentley *et al.* [12] using the Davidson-Jones (DJ) wave function.

of hydrogen was absolutized by taking into account the different target densities (pressure) of hydrogen and helium. A similar normalization method was also used in our previous paper [11]. The resolution of momentum transfer is about 0.091 a.u., which is due to the finite size of the solid angle viewed by the analyzer. The experimental errors of $\zeta(\mathbf{q})$ are attributed to the statistics of counts, the normalizing procedure, as well as the fitting procedure, which are also shown in Fig. 2.

It can be seen clearly from Fig. 2 that the present experimental results are in excellent agreement with the calculation of Bentley *et al.* [12] using the Davidson-Jones wave function, which is essentially an expansion of the exact ground-state wave function of Kolos and Roothaan [24]. It should be emphasized that x-ray elastic scattering is a photon-in photon-out process, and the theoretical description of the photon-target interaction is expressed in the $\mathbf{A}^2$ term of the corresponding interaction Hamiltonian [17], where $\mathbf{A}$ is a photon vector potential, so only the coupling of the photon with the electrons in the target should be accounted for. There is no contribution of nuclei to the scattering amplitude according to Eq. (4), which shows the obvious advantages of the high-resolution x-ray elastic scattering method. In other words, only the electronic properties of the target can be explored by the high-resolution x-ray elastic scattering method, which is completely different from the high-energy electron impact method, although the latter is generally thought to be a powerful tool to study the electronic structure of atoms or molecules.

For a sufficiently fast electron collision with an atom or molecule in which the first Born approximation (FBA) is valid [18,25,26], the elastic differential cross section $(\frac{d\sigma}{d\Omega})_e$ can be expressed as

$$\left(\frac{d\sigma}{d\Omega}\right)_e = (2\pi)^{-2}\frac{q_f}{q_i}\left|\int \exp(i\mathbf{q}\cdot\mathbf{r})\Psi_0^*(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{R}) \times V\Psi_0(\mathbf{r}_1,\ldots,\mathbf{r}_N;\mathbf{R})d\mathbf{r}_1\cdots d\mathbf{r}_N d\mathbf{r}\right|^2, \quad (5)$$

where

$$V = -\sum_{j=1}^{Z}\frac{1}{|\mathbf{r}-\mathbf{r}_j|} + \frac{1}{|\mathbf{r}-\mathbf{R}_a|} + \frac{1}{|\mathbf{r}-\mathbf{R}_b|}, \quad (6)$$

$\mathbf{R}_a$ and $\mathbf{R}_b$ are the position vectors of the nuclei, and $R = |2R_a| = |2R_b|$ is the internuclear distance for molecular hydrogen. $\mathbf{r}$ is the position of the incident electron. Then the differential cross section of the elastic scattering of electrons from hydrogen can be written as

$$\begin{aligned}\left(\frac{d\sigma}{d\Omega}\right)_e &= 4\left(\frac{q_f}{q_i}\right)q^{-4}\left|\langle\Psi_0|\exp(i\mathbf{q}\cdot\mathbf{R}_a) + \exp(i\mathbf{q}\cdot\mathbf{R}_b) - \sum_{i=j}^{2}\exp(i\mathbf{q}\cdot\mathbf{r}_j)|\Psi_0\rangle\right|^2 \\ &= \frac{1}{\pi}\left(\frac{q_f}{q_i}\right)q^{-4}\iint \sin\theta d\theta d\varphi\left|\int\Psi_0^*(R) \times[2\cos(\mathbf{q}\cdot\mathbf{R}/2) - \varepsilon_0(\mathbf{q};R,\theta,\varphi)]\Psi_0(R)dR\right|^2. \quad (7)\end{aligned}$$

Since $\cos(\mathbf{q}\cdot\mathbf{R}/2)$ as well as $\varepsilon_0(\mathbf{q};R,\theta,\varphi)$ are functions of the internuclear distance R and the angle between $\mathbf{q}$ and $\mathbf{R}$, it can be seen clearly from Eq. (7) that the interference term prevents one from extracting the pure electronic structure information about the ground state of the molecule from the experimental elastic differential cross section of high-energy electron scattering, which is a unique merit of the aforementioned high-resolution x-ray-scattering method. For molecular hydrogen, we can give a quantitative estimation of the interference term. As an approximation, we neglect the vibration effect and fix $R = \mathcal{R}_e$, with $\mathcal{R}_e$ being the equilibrium internuclear distance. Then, by using the elastic squared form factor of x-ray scattering calculated by Ref. [12] and the differential cross sections of electron elastic scattering calculated by Ref. [27], as well as the analytic term of the pure nuclear scattering term, the interference term can be determined according to Eq. (7) and is shown in Fig. 3.

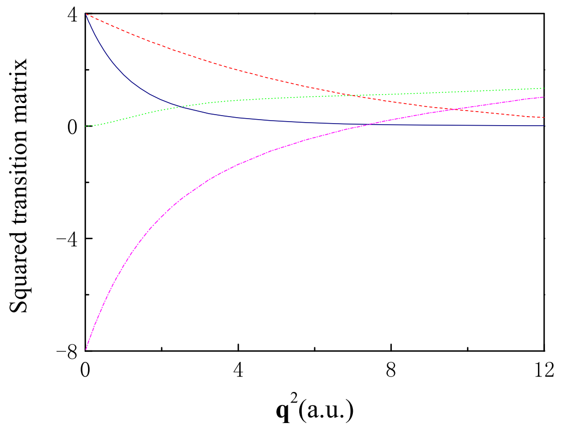

FIG. 3. (Color online) Dotted (green) line: The squared matrix element of fast electron scattering calculated by Ford *et al.* [27]. Solid (navy) line: The elastic squared form factor $\zeta(\mathbf{q})$ of x-ray scattering calculated by Bentley *et al.* [12]. Dashed (red) line: The squared analytic term of the pure nuclear scattering term. Dashed-dotted (magenta) line: The interference term.

It can be seen clearly that this interference term is very important. It should be mentioned that for the excitation processes of the atom or molecule, the high-energy electron scattering method and high-resolution x-ray-scattering method are similar and both of them are free from nuclear scattering due to the orthogonality of the initial and final wave functions, as noticed in Refs. [8,10], which is different from the elastic scattering.

In summary, high-resolution x-ray elastic scattering is used to study the dynamic parameters of atoms and molecules in the gas phase, and the elastic squared form factor $\zeta(\mathbf{q})$ of molecular hydrogen is determined. The present experimental results match the theoretical calculation very well, and pure electronic structure information about the ground state of hydrogen is obtained, which cannot be determined by the traditional high-energy electron scattering method due to the interference between the scattering amplitude from separate nuclei and of the electrons in the target. The present work shows that high-resolution x-ray scattering has unique advantages to determine the electronic structure information about the ground state of molecules, especially for the polyatomic molecules, due to the complex skeletal structure of the nuclei. We have reason to believe that high-resolution x-ray scattering has extensive applicability in determining the electronic structure of the ground state of molecules in the future.

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[1] M. F. Reedijk, J. Arsic, F. F. A. Hollander, S. A. de Vries, and E. Vlieg, Phys. Rev. Lett. **90**, 066103 (2003).
[2] A. Zouni, H. T. Witt, J. Kern, P. Fromme, N. Krauss, W. Saenger, and P. Orth, Nature (London) **409**, 739 (2001).
[3] J. Rahuel, V. Rasetti, J. Maibaum, H. Rüeger, R. Göschke, N. C. Cohen, S. Stutz, F. Cumin, W. Fuhrer, J. M. Wood *et al.*, Chem. Biol. **7**, 493 (2000).
[4] C. T. Chantler, J. Phys. Chem. Ref. Data **29**, 597 (2000).
[5] F. Smend and H. Czerwinski, Z. Phys. D **1**, 139 (1986).
[6] F. Smend, D. Schaupp, H. Czerwinski, M. Schumacher, A. H. Millhouse, and L. Kissel, Phys. Rev. A **36**, 5189 (1987).
[7] D. R. Chipman and L. D. Jennings, Phys. Rev. **132**, 728 (1963).
[8] B. P. Xie, L. F. Zhu, K. Yang, B. Zhou, N. Hiraoka, Y. Q. Cai, Y. Yao, C. Q. Wu, E. L. Wang, and D. L. Feng, Phys. Rev. A **82**, 032501 (2010).
[9] L. F. Zhu, W. Q. Xu, K. Yang, Z. Jiang, X. Kang, B. P. Xie, D. L. Feng, N. Hiraoka, and K. D. Tsuei, Phys. Rev. A **85**, 030501(R) (2012).
[10] L. F. Zhu, L. S. Wang, B. P. Xie, K. Yang, N. Hiraoka, Y. Q. Cai, and D. L. Feng, J. Phys. B **44**, 025203 (2011).
[11] X. Kang, K. Yang, Y. W. Liu, W. Q. Xu, N. Hiraoka, K. D. Tsuei, P. F. Zhang, and L. F. Zhu, Phys. Rev. A **86**, 022509 (2012).
[12] J. J. Bentley and R. F. Stewart, J. Comput. Phys. **11**, 127 (1973).
[13] J. J. Bentley and R. F. Stewart, J. Chem. Phys. **62**, 875 (1975).
[14] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962).
[15] J. A. Bradley, G. T. Seidler, G. Cooper, M. Vos, A. P. Hitchcock, A. P. Sorini, C. Schlimmer, and K. P. Nagle, Phys. Rev. Lett. **105**, 053202 (2010).
[16] J. A. Bradley, A. Sakko, G. T. Seidler, A. Rubio, M. Hakala, K. Hamalainen, G. Cooper, A. P. Hitchcock, K. Schlimmer, and K. P. Nagle, Phys. Rev. A **84**, 022510 (2011).
[17] W. Schülke, *Electron Dynamics by Inelastic X-Ray Scattering* (Oxford Science, Oxford, UK, 2007).
[18] M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971).
[19] R. H. J. Jansen, F. J. de Heer, H. J. Luyken, B. van Wingerden, and H. J. Blaauw, J. Phys. B **9**, 185 (1976).
[20] J. P. Bromberg, J. Chem. Phys. **61**, 963 (1974).
[21] N. M. Cann and A. J. Thakkar, J. Electron. Spectrosc. Relat. Phenom. **123**, 143 (2002).
[22] X. J. Liu, L. F. Zhu, Z. S. Yuan, W. B. Li, H. D. Cheng, J. M. Sun, and K. Z. Xu, J. Electron. Spectrosc. Relat. Phenom. **135**, 15 (2004).
[23] X. Y. Han and J. M. Li, Phys. Rev. A **74**, 062711 (2006).
[24] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).
[25] H. Bethe, Ann. Phys. **5**, 325 (1930).
[26] H. Bethe, Z. Phys. **76**, 293 (1930).
[27] A. L. Ford and J. C. Browne, Chem. Phys. Lett. **20**, 284 (1973).