Probing the two-electron cusp in the ground states of He and H₂

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We report on kinematically complete measurements and ab initio non-perturbative calculations of double ionization of He and H₂ by a single 800 eV circularly polarized photon. We utilize the quasi-free mechanism of photoionization to probe the two-electron cusp in the ground state of these two targets. Our approach constitutes a new method of electron localization by studying dynamic many-electron correlation and provides valuable insight into the mechanisms of non-dipole photoionization.

Many-electron correlations in atoms and molecules have been a subject of intense theoretical and experimental scrutiny [1]. In coordinate space, many-particle wave functions feature the so-called cusps, which are configurations where two particles occupy the same position. The electron-nucleus cusp is the most prominent one [2]. It has a major influence on the total binding energy of the system and is well tested by spectroscopic means. The two-electron cusp is much more subtle. Only few highly correlated ground-state wave functions display this cusp correctly (3 [4]) and traditional photoionization studies are not capable of probing it, because the singular point in phase space barely contributes to the total cross section. Indeed, at high (but non-relativistic) energies, the Born approximation demonstrates how the dependence of the cross section on the photon energy ω characterizes the initial spatial probability density of electrons relative to the nucleus [5]. Accordingly, the total single ionization cross section σ⁺ scales as Z²/ω⁷/² for hydrogen-like 1S orbitals with Z being the nuclear charge. For two-electron targets, double ionization is facilitated by electron-electron correlation via the shake-off (SO) and two-step-one (TS1) processes [6]. At high photon energies, the ratio of double-to-single ionization probabilities σ²⁺/σ⁺ converges to the so-called shake-off limit, where two-step-one no longer plays a role [7]. In this limit, the SO probability becomes a constant fraction of the single ionization cross section. However, as single ionization is a precursor to SO, this two-electron correlation process also probes the spatial probability density of electrons relative to the nucleus.

It had been predicted by Amusia et al. [8] that under certain kinematic conditions, the quasi-free mechanism (QFM) facilitates double ionization without any involvement of the nucleus. QFM leads to the creation of a quasi-free electron pair that is emitted back-to-back with equal energy sharing. Accordingly, the nucleus is only a spectator, remaining nearly at rest because the inter-electron degree of freedom absorbs the energy and momentum of the photon. The QFM probability is related to the initial spatial probability density of electrons relative to each other, the so-called intracule h(r⁻), r⁻ being the inter-electronic distance [9]. Note that the intracule is the square modulus of the intracule wave function. Because the QFM is most efficient when the two electrons are located close to each other, it probes h(r⁻ = 0) and hence the two-electron cusp in the ground state of a two-electron target. The QFM was confirmed experimentally in the helium atom by Schöffler et al. [10]. As the ground-state wave functions of He and H₂ both have the same 1S symmetry, the back-to-back emission at equal energy sharing is forbidden by a dipole selection rule [11]. Therefore, the QFM is a pure quadrupole contribution to one-photon double ionization (PDI) and it can be isolated particularly clearly in a fully differential cross section [12]. In the present work, we have used this experimental access to confirm the quasi-free mechanism for the H₂ molecule irradiated with 800 eV circularly polarized photons.

In our experiments, we employed a COLTRIMS (Cold Target Recoil Ion Momentum Spectroscopy) reaction microscope [13–15] and intersected a supersonic jet of the respective target gas with a synchrotron beam of 800 eV circularly polarized photons from beamline P04 at PETRA III (DESY, Hamburg [16]). In order to increase the photon flux to an estimated 1.6 × 10¹⁴ photons/s maximum, we used a so-called pink beam by setting the monochromator to zeroth order. Additionally, an aluminium blank mirror was used instead of the usual monochromator gratings of beamline P04. To exclude low-energy photons, a foil filter was inserted into the beam path. The reaction fragments from the interaction region were guided by electric and magnetic fields towards two time- and position-sensitive detectors.
Apart from one electron, we detect all the reaction fragments in coincidence and calculate their three-dimensional momentum vectors from the times-of-flight and positions-of-impact. The missing electron’s momentum vector is calculated using momentum conservation. This procedure is less accurate for H$_2$, as the center of mass has to be calculated from two protons instead of being directly measured via the doubly charged He nucleus. Thus, the systematic error propagating to the calculated electron is larger and the noise reduction (exploiting energy conservation) is less efficient in case of H$_2$. The different signal-to-noise ratios explain why the agreement between experient and theory is better for He than for H$_2$ in this work.

To search for the QFM fingerprint, the electron mutual angle $\alpha = \angle(k_1, k_2)$ is analysed along with the electron energy sharing calculated as $\Delta E = E_1/(E_1 + E_2)$. Here $k_1,2$ and $E_1,2$ are the momentum vectors and the kinetic energies of the electrons 1 and 2, respectively. Figures 1 (a) and (b) show the measured doubly differential cross sections (DDCS) $[d^2\sigma(\Delta E, \alpha)/d\Delta E d\alpha]$ for PDI of H$_2$ and He by a single 800 eV circularly polarized photon. The events resulting from QFM are located around equal energy sharing ($\Delta E = 0.5$) and back-to-back emission ($\cos \alpha = -1$). In comparison to the other features, QFM is more intense in He than in H, suggesting a higher ratio $\sigma_{\text{QFM}} / \sigma^{2\pi}$ in the former target (note that the QFM contribution for He can only be seen against the SO background with a logarithmic scale display).

However, the absolute cross sections cannot be retrieved from the experimental data and therefore measured differential cross sections for H$_2$ and He cannot be inter-normalized from these datasets alone. This can be achieved by numerical computations using the external complex scaling method in the prolate spheroidal coordinates (PSECS) [19]. Said ab initio method is based on a solution of the six-dimensional driven Schrödinger equation,

$$\hat{\mathit{H}}_0 - E) \Psi^{(+)}(r_1, r_2) = -\hat{\mathit{H}}_{\text{int}} \Phi_0(r_1, r_2),$$

(1)

for the first order function $\Psi^{(+)}(r_1, r_2)$ with a boundary condition for the outgoing wave, where $r_{1,2}$ are the position vectors for electrons 1 and 2 with respect to the nucleus. $\hat{\mathit{H}}_0$ is an unperturbed two-electron Hamiltonian in the field of the two fixed nuclei and $\Phi_0(r_1, r_2)$ is the initial-state electronic wave function. Earlier, PSECS has been applied for calculations of dipole PDI [19, 20]. Presently, the quadrupole interaction is also included in $\hat{\mathit{H}}_{\text{int}}$. Figures 1 (c) and (d) show the calculated DDCS for PDI of H$_2$ and He, that are in excellent agreement with the experimental results. PSECS calculated total integrated cross sections are listed in Table 1.

With the kinematically complete experimental data and ab initio calculations, we can examine the differences in the correlated structure of the ground states of He and H$_2$. Figure 2 presents a singly differential cross section (SDCS) for PDI of He and H$_2$, for events from the QFM-dominated range of the electron mutual angle ($\alpha = 180^\circ \pm 30^\circ$) and resolved for the energy sharing between the two electrons $\Delta E$. The two theory curves share the same absolute scale and the experimental data are normalized to theory at the equal energy sharing point. The peak distributions around equal energy sharing represent the QFM without any involvement of the nucleus. Hence, the strength of the equal energy peak relates to the electron-electron pair density $h(0)$ in the ground-state wave functions of He and H$_2$. Contrastingly, an asymmetric energy sharing requires the nucleus to compensate the recoil of the two emitted electrons which is imparted by the SO process. This process dominates the total integrated cross sections of He and H$_2$ PDI at 800 eV photon energy [23]. In SO, PDI proceeds through the quasi-instantaneous removal of the first electron, whereas the second electron cannot relax adiabatically to the singly charged ionic ground state. Instead, the secondary electron is either shaken up to a discrete excitation or shaken off to the continuum. For SO photoionization, a small energy transfer, i.e. a very unequal energy sharing, is strongly favored and the slow electron is emitted almost isotropically [23]. Thus, the probability of SO photoionization depends only weakly on the electron mutual angle $\alpha$. As SO transfers a substantial recoil to the ions, it depends on the electron position relative to the center of
mass, described by the so-called extracule wave function \[\Phi_0(r_+, r_-) = \chi_0(r_+)\psi_0(r_-)\].

Here \(r_-\) and \(k\) describe the relative electron motion whereas \(r_+\) and \(K\) are related to the electron-pair center of mass. In these variables, the transition operator is transformed into

\[
\hat{H}_{\text{int}} = \epsilon \cdot r_+ + i(\epsilon \cdot r_+) (k_\gamma \cdot r_+) + \frac{i}{4} (\epsilon \cdot r_-)(k_\gamma \cdot r_-).
\]

The first term is the electric dipole (E1) contribution to the transition amplitude, the second and third term contain the electric quadrupole (E2) contribution. While the dipole acts only on the “+” coordinate, transferring the recoil to the center of mass, the part of the quadrupole

\[
\hat{H}_- = \frac{ik_\gamma}{4} (\epsilon \cdot r_-)(n_\gamma \cdot r_-)
\]

acts directly on the inter-electron separation (the “−” coordinate). When the electrons are emitted back-to-back with equal energy, they balance each other’s momentum. Accordingly, as nuclear recoil is not involved, this part of the quadrupole contribution is responsible for the QFM.

For a qualitative analysis, we consider the ground-state wave function of the two electrons in the following form

\[
\Phi_0(r_+, r_-) = \chi_0(r_+)\psi_0(r_-).
\]

Here the ground-state wave function of relative motion (the intracule wave function) is

\[
\psi_0(r_-) = A_0 \exp[r_-/2 - r_-^2/b^2],
\]

and \(\chi_0(r_+)\) is the extracule wave function. The intracule wave function is chosen to satisfy the cusp condition at \(r_- \to 0\). The Gaussian multiplier with the cut-off parameter \(b\) is introduced to compensate an infinite growth of the exponential multiplier as \(r_- \to \infty\). As shown in Fig. 3, the intracule \(h(r_-) = |\psi_0(r_-)|^2\) has the form of a shifted Gaussian which approximates the intracules of He (25) and \(H_2\) (26).

Accordingly, the amplitude of the QFM process can be written in the form

\[
f_{\text{QFM}} = \langle e^{ik_1 r_1 + i k_2 r_2} |\hat{H}_-| \Phi_0 \rangle = \frac{ik_\gamma}{4} f_+(K)f_-(k),
\]

where

| (barn)          | Single ionization | Dipole          | Double ionization | Quadrupole          | QFM              |
|-----------------|-------------------|-----------------|-------------------|---------------------|------------------|
|                  | Present Ref. [22] | Present Ref. [21] | Present Ref. [21] | Present Ref. [21] | Present Ref. [10] |
| He              | 730               | 784             | 0.10              | 1.21                | 0.00539          | 0.02             |
| H_2             | 62                | 71              | 0.75              | 0.015               | 0.00105          |                  |

FIG. 2. Singly differential cross sections \(d\sigma(\Delta E)/d\Delta E\) for PDI of \(H_2\) and He by a single 800 eV circularly polarized photon for electrons emitted back to back (theory and experimental data are integrated over \(\alpha = 180^\circ \pm 30^\circ\)). The experimental datasets are normalized to theory at the equal energy sharing point. The colored areas under the theory curves represent the QFM cross sections tabulated in Table I. The ratio of the areas is \(\sigma^2_{\text{QFM}}(\text{He})/\sigma^2_{\text{QFM}}(\text{H}_2) = 5.13\).
region $K < K_{QFM}$, where QFM dominates, we should get the desired PICSI. To express the PICSI in terms of electron energy sharing and mutual angle we cast it in the form

$$
\zeta = \int_0^{\delta_{QFM}} \int_{-1}^1 \frac{\sigma^2(\Delta E, \alpha) w(\kappa, \beta, \eta) J(\beta, \eta)}{\rho(\kappa, \beta, \eta, \eta_{QFM})} \eta_{QFM} \mathrm{d}\eta \mathrm{d}\beta ,
$$

(11)

where $\sigma^2(\Delta E, \alpha) = d^2 \sigma(\Delta E, \alpha) / d\Delta E d\alpha$. Here we use the shorthand $\eta = \cos \alpha$, $\beta = \Delta E / E$ and introduce $\eta_{QFM}$ and $\beta_{QFM}$ as substitutes of $K_{QFM}$ in confining the QFM-dominated area of the cross section. We also rewrite $\rho(k, K)$ in the form $\rho(\kappa, \beta, \eta_{QFM}) = \sqrt{1 - (1 - \kappa^2) \eta_{QFM}^2}$, where $\kappa = K^2 / 4E$ and $\eta_{QFM} = \cos \theta_{QFM} = (k \cdot K) / (kK)$. Furthermore, we add the weight factor $w(\kappa) = \max \left( 1, \kappa \eta_{QFM} \right)$ and the Jacobian $J(\beta, \eta) = \frac{1}{2K(\beta, \eta)} E \left( \frac{\eta}{\eta_{QFM}} \right)^{-1} \sqrt{1 - \beta^2}$. Once integrated, Eq. (11) yields $\zeta_{He} / \zeta_{H_2} = 4.7$. This result suggests that $h(0)$ is roughly 4.7 times higher for He than for $H_2$ which is considerably close to the ratio of 6.1 as obtained by the intracules of [25] (He) and [26] (H$_2$).

Up to now, we considered $H_2$ at the average internuclear distance of $R = 1.4$ au. In the reflection approximation, $R$ is related to the kinetic energy release (KER) via KER = 1/R (in atomic units). Hence, we can investigate differential cross sections depending on $R$ by inspecting subsets of our data for which the KER is in a certain range, as shown in Fig. 4. Note that He corresponds to an inter-nuclear distance $R = 0$. The experimental datasets in Fig. 4 are inter-normalized at the highly asymmetric energy sharing fringes. By increasing $R$, the probability of the QFM peak at the energy
sharing midpoint grows relatively to the fringes. This finding suggests the following explanation: As $R$ grows, both electrons stay closer to the center of mass in the middle of the two protons while the electron proximity to the nuclei decreases. The inter-electron distance is barely affected by this expansion and the system accessibility for QFM photoionization remains unaffected. On the other hand, SO photoionization is less likely to happen as the recoil momentum exchange with the nucleus is hampered.

In conclusion, the QFM mechanism of PDI in the high photon energy regime allows studying the fine details of inter-electron correlation in the two-electron atomic and molecular targets. Similarly to single photoionization, which reveals the one-electron charge density, the QFM opens experimental access to the electron pair density or the squared intracule wave function. This is important for several reasons. Firstly, it provides a rigorous test to various theoretical models dealing with many-electron correlation. Secondly, accurate charge densities and intracules are needed for evaluation of x-ray scattering form-factors and intensities. The latter can be computed from the Fourier transforms of $h(r−)$ \[27\] \[28\].

Finally, nearly 50 years since the theoretical prediction of QFM \[8\], not only has it been confirmed experimentally, but has also become a novel tool for many-electron spectroscopy of correlated states of matter.

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[1] D. R. Yarkony. *Modern Electronic Structure Theory*. World Scientific Publishing, Singapore, 1995.
[2] T. Kato. On the eigenfunctions of many-particle systems in quantum mechanics. *Commun. Pure Appl. Math.*, 10 (2):151–177, 1957.
[3] E. A. Hylleraas. Über den Grundterm der Zweielektronenprobleme von H-, He, Li+, Be++ usw. *Z. Physik*, 65 (3):209, 1930.
[4] H. M. James and A. S. Coolidge. A Correction and Addition to the Discussion of the Ground State of H2. *J. Chem. Phys.*, 32(2):129–130, 1935.
[5] H. A. Bethe and E. E. Salpeter. *Quantum Mechanism of One- and Two-Electron Atoms*. Springer, Berlin, 1957.
[6] J. H. McGuire. *Electron Correlation Dynamics in Atomic Collisions*. Cambridge University Press, Cambridge, 1997.
[7] T. Aberg. Asymptotic Double-Photoexcitation Cross Section of the Helium Atom. *Phys. Rev. A*, 2(5):1726, 1970.
[8] M. Ya. Amusia, E. G. Drukarev, V. G. Gorshkov, and M. O. Kazachkov. Two-electron photoionization of helium. *J. Phys. B: At. Mol. Opt. Phys.*, 8:1248, 1975.
[9] A. S. Eddington. *Fundamental Theory*. Cambridge University Press, Cambridge, 1946.
[10] M. S. Schöffler, C. Stuck, M. Waizt, F. Trinter, T. Jahnke, U. Lenz, M. Jones, A. Bellačem, A. L. Landers, M. S. Pindzola, C. L. Cocke, J. Colgan, A. Kheifets, I. Bray, H. Schmidt-Böcking, R. Dörner, and Th. Weber. Ejection of quasi-free-electron pairs from the helium-atom ground state by single-photon absorption. *Phys. Rev. Lett.*, 111:013003, 2013.
[11] F. Maulbetsch and J. S. Briggs. Selection rules for transitions to two-electron continuum states. *J. Phys. B: At. Mol. Opt. Phys.*, 28:551, 1995.
[12] S. Grundmann, F. Trinter, A. W. Bray, S. Eckart, J. Rist, G. Kastirke, D. Metz, S. Klumpp, J. Vielhaus, L. Ph. H. Schmidt, J. B. Williams, R. Dörner, T. Jahnke, M. S. Schöffler, and A. S. Kheifets. Separating Dipole and Quadrupole Contributions to Single-Photon Double Ionization. *Phys. Rev. Lett.*, 121(17):173003, 2018.
[13] R. Dörner, V. Mergel, O. Jagutzki, L. Spielbergger, J. Ulrich, R. Moshammer, and H. Schmidt-Böcking. Cold Target Recoil Ion Momentum Spectroscopy: a 'momentum microscope' to view atomic collision dynamics. *Phys. Rep.*, 330:95, 2000.
[14] J. Ulrich, R. Moshammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking. Recoil-ion and electron momentum spectroscopy: reaction-microscopes. *Rep. Prog. Phys.*, 66:1463, 2003.
[15] T. Jahnke, Th. Weber, T. Osipov, A. L. Landers, O. Jagutzki, L. Ph. H. Schmidt, C. L. Cocke, M. H. Prior, H. Schmidt-Böcking, and R. Dörner. Multicoincidence studies of photo and Auger electrons from fixed-in-space molecules using the COLTRIMS technique. *J. Electron Spectrosc. Relat. Phenom.*, 141:229, 2004.
[16] J. Viefhaus, F. Scholz, S. Deinert, L. Glaser, M. Ilchen, J. Seltmann, P. Walter, and F. Siewert. The Variable Polarization XUV Beamline P04 at PETRA III : Optics, mechanics and their performance. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 710:151, 2013.
[17] O. Jagutzki, J. S. Lapington, L. B. C. Worth, U. Spillman, V. Mergel, and H. Schmidt-Böcking. Position sensitive anodes for MCP read-out using induced charge measurement. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 477:256, 2002.
[18] O. Jagutzki, V. Mergel, K. Ullmann-Pfleger, L. Spielbergger, U. Spillmann, R. Dörner, and H. Schmidt-Böcking. A broad-application microchannel-plate detector system for advanced particle or photon detection tasks: large area imaging, precise multi-hit timing information and high detection rate. *Nucl. Instrum. Methods Phys. Res., Sect. A*, 477:244, 2002.
[21] J. A. Ludlow, J. Colgan, T.-G. Lee, M. S. Pindzola, and F. Robicheaux. Double photoionization of helium including quadrupole radiation effects. *J. Phys. B: At. Mol. Opt. Phys.*, 42:225204, 2009.

[22] M. Yan, H. R. Sadeghpour, and A. Dalgarno. Photoionization Cross Sections of He and H2. *Astrophys. J.*, 496:1044–1050, 1998.

[23] A. Knapp, A. Kheifets, I. Bray, Th. Weber, A. L. Landers, S. Schössler, T. Jahnke, J. Nickles, S. Kammer, O. Jagutzki, L. Ph. H. Schmidt, T. Osipov, J. Rösch, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner. Mechanisms of photo double ionization of helium by 530 eV photons. *Phys. Rev. Lett.*, 89:033004, 2002.

[24] R. Dörner, J. M. Feagin, C. L. Cocke, H. Bräuning, O. Jagutzki, M. Jung, E. P. Kanter, H. Khemliche, S. Kravis, V. Mergel, M. H. Prior, H. Schmidt-Böcking, L. Spielberger, J. Ullrich, M. Unversagt, and T. Vogt. Fully differential cross sections for double photoionization of he measured by recoil ion momentum spectroscopy. *Phys. Rev. Lett.*, 77(6):1024–1027, 1996.

[25] A. J. Thakkar and V. H. Smith Jr. Accurate charge densities and two-electron intracule functions for the heliumlike ions. *J. Chem. Phys.*, 67(3):1191–1196, 1977.

[26] T. Koga and K. Matsui. Optimal Hylleraas wave functions. *Z. Phys. D Atom. Mol. Cl.*, 27(2):97–102, 1993.

[27] R. Benesch and V. H. Smith Jr. Correlation and X-ray scattering. I. Density matrix formulation. *Acta Crys. A*, 26(6):579–586, 1970.

[28] A. J. Thakkar and V. H. Smith Jr. The electron electron cusp condition for the spherical average of the intracule matrix. *Chem. Phys. Lett.*, 42(3):476, 1976.