The Quadruplon in a Monolayer Semiconductor

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Abstract

Understanding the structure of matter and interaction or correlations among the constituent elementary particles are the central tasks of all branches of science, from physics, chemistry, to biology. In physics, this ultimate goal has spurred a constant search for high-order correlated entities or composite particles for nearly all states and forms of matter, from elementary particles, nuclei, cold atoms, to condensed matter. So far, such composite particles involving two or three constituent particles have been experimentally identified, such as the Cooper pairs, excitons, and trions in condensed matter physics, or diquarks and mesons in quantum chromodynamics. Although the four-body irreducible entities have long been predicted theoretically in a variety of physical systems alternatively as quadruplons1, quadrons2, or quartets3, the closely related experimental observation so far seems to be restricted to the field of elementary particles (e.g. the recent tetraquark at CERN4). In this article, we present the first experimental evidence for the existence of a four-body irreducible entity, the quadruplon, involving two electrons and two holes in a monolayer of Molybdenum Ditelluride. Using the optical pump-probe technique, we discovered a series of new spectral features that are distinct from those of trions and bi-excitons. By solving the four-body Bethe-Salpeter equation in conjunction with the cluster expansion approach, we are able to explain these spectral features in terms of the four-body irreducible cluster or the quadruplons. In contrast to a bi-exciton which consists of two weakly bound excitons, a quadruplon consists of two electrons and two holes without the presence of an exciton. Our results provide experimental evidences of the hitherto theorized four-body entities and thus could impact the understanding of the structure of matter in a wide range of physical systems or new semiconductor technologies.
Main

Whereas the search for the most “elementary” constituent particles of matter has been a never-ending pursuit in high-energy physics, the understanding of the interactions or correlations among these particles dominates studies in lower energy scales that are more relevant to our daily experience and technology. Such interactions lead to the formation of correlated entities or composite particles that determine the basic material properties, underlie our fundamental understanding of almost all fields of physical and material sciences, and provide the foundation for all modern technologies. In condensed matter physics, correlated entities, such as excitonic complexes: excitons (X), trions (T), and bi-excitons (BX), are critical to our understanding of the basic material properties, and especially to the ever-richer physics of the celebrated Mott transition beyond the simple exciton-plasma picture. Recently, higher-order correlated entities have attracted much interests, including the Bose-Einstein condensation (BEC)\(^5\), BEC-BCS crossover via different bosonizations of Fermions in strongly correlated systems, or dropletions\(^5\)\(^-8\) in semiconductors. It was shown theoretically that the formation of the quadron was more favorable than the bi-exciton in a strongly confined parabolic quantum dot\(^2\). In superconductivity theories, the charge-4e configuration was proposed as an alternative to the conventional Cooper-pair mechanism\(^3\)\(^,9\). Multiplons (including quadruplons) were also recently studied theoretically in the 1D Hubbard model\(^1\). In elementary particle physics, various four-quark configurations have been proposed theoretically, such as the tetraquark, the diquark-antidiquark, and those in the meson-meson model\(^10\). The most recent experiment at CERN seemed to confirm that the tetraquark corresponds to the longest-living four-quark configuration\(^4\). To date, experimental evidence for the existence of such a 4B irreducible cluster (or entity) is still lacking in other field beyond the high-energy physics.

Two-dimensional (2D) layered semiconductors, such as monolayer transition metal dichalcogenides (ML-TMDCs), provide a unique platform for the study of high-order correlated entities or excitonic complexes. The reduced dielectric screening in ML-
TMDCs leads to extremely large exciton binding energies\textsuperscript{11,12} and much more stable high-order excitonic complexes than those in conventional semiconductors. Indeed, trions\textsuperscript{13,14}, bi-excitons\textsuperscript{15-19}, and even charged bi-excitons\textsuperscript{20-24} were experimentally observed in such ML-TMDCs with larger binding energies and at higher temperatures than those in bulk semiconductors. In addition, the unique spin-valley locking\textsuperscript{25,26} leads to more varieties of the correlated entities than in conventional semiconductors. For the same reason, the correlated entities with specific spin-valley polarizations are addressable by choosing the helicity of the pump or probe light\textsuperscript{18,19}. The combined unique features described above have never before been available for the study of these correlated entities.

To take advantages of these unprecedented opportunities, we conducted a combined theoretical and experimental investigation into the possible existence of higher-order correlated complexes in ML-TMDCs beyond the known trions and bi-excitons (including those that are reducible to excitons, trions, or bi-excitons). Using the helicity-resolved pump-probe technique, we observed a series of unexpected spectral features in the transient reflectance in a wide range of probe photon energies well below the T resonances in gate-controlled monolayer molybdenum ditelluride (ML-MoTe\textsubscript{2}) samples. Up to six spectral peaks were revealed, extending over 40 meV from below T all the way up to X. These spectral features cannot be attributed to familiar origins such as defects or phonon-related processes. To understand the new spectral features, we developed a perturbation theory based on the 4-body Bethe-Salpeter equation (4B-BSE) for the two-electron-two-hole (2e2h) system. By recasting the Feynman diagrams of the 4B-BSE into the cluster expansion formalism, we are able to compare the spectral contributions of the irreducible clusters of various orders up to the 4\textsuperscript{th}. Interestingly, we show that the clusters corresponding to the trions and bi-excitons cannot produce most of the new spectral features, thus excluding the trions and bi-excitons as their origin. Importantly, our theory-experiment comparison shows that the 4\textsuperscript{th}-order irreducible 2e2h-cluster, or quadruplon, is necessary and sufficient in producing all the experimental spectral features, thus providing experimental
verification of the existence of the quadruplons.

Four-body interactions and the cluster expansion

The most natural way of visualizing correlated entities of various orders and associated many-body interactions is through the cluster expansion method\textsuperscript{27}. This theoretical method has more recently been proven successful in describing the high-order excitonic correlations in e-h droplets\textsuperscript{6,7}. Generalizing such cluster expansion of excitons to the case of individual electrons and holes with the spin degree of freedom, we can write down the complete sequence of irreducible clusters for the 2e2h system as in Fig. 1a – 1c. The specialization of such cluster expansion for ML-MoTe\textsubscript{2} leads to the similar sequence of clusters, now expressed together with the band structures in Fig. 1d & 1e. \( \triangle \) represents an irreducible cluster of the \( n \)th-order with \( n \) Fermions.

Clearly \( \triangle \) is a quasi-free electron or hole. \( \triangle \) represents a direct or indirect e-h pair, or 2-body (2B) state, including all the excitonic Rydberg states: 1s-X, 2p-X, 2s-X, .... \( \triangle \) represents an e-e-h or e-h-h 3-body (3B) state. In the language of multiplons proposed by Rausch \textit{et al}\textsuperscript{1}, \( \triangle \), \( \triangle \), and \( \triangle \) are doublon, triplon, and quadruplon, respectively. Each time we include one more cluster of higher order into a truncated expansion, it re-introduces weak interactions among irreducible clusters of all the lower orders. Such interactions are indicated by the wavy lines in Fig. 2a (see Methods S1, Extended Data Fig. 1, for the discussions about the origin of such weak interactions). Here, we truncated the cluster expansion up to the 4th order. As a result, the original non-interacting cluster \( \triangle \) (see also Extended Data Fig. 1d) becomes weakly interacting, \textit{i.e.} \( \triangle \sim \triangle \) (see Extended Data Fig. 1f), representing a bi-exciton (1s-X) \( \sim \) (1s-X) including all its excited states such as (1s-X) \( \sim \) (2p-X), (1s-X) \( \sim \) (2s-X) .... Obviously, cluster \( \triangle \) or quadruplon (or quadron\textsuperscript{2}) represents generally a distinct physical entity than the bi-exciton \( \triangle \sim \triangle \).
the lack of a clear association of any one of the two electrons to a given hole. But it is easy to imagine that a certain disassociation event (e.g. an excitation) of a quadruplon could lead to the formation of a bi-exciton. In this sense, a bi-exciton can be an excited state of a quadruplon (see Fig. 5g and Extended Data Fig. 16 for a comparison of various states in the $2e2h$ system). We point out that the fine structure of bi-excitons was studied recently as a result of the $e$-$h$ exchange interaction$^{19,28}$. 
Fig. 1 | A cluster expansion picture of a four-body system. a, Decomposition of the 2e2h 4B system into three parts according to the time reversal (K ↔ K') symmetry, as indicated by the blue-red symmetry of the square boxes. The first two terms/boxes are mutually exchanged under the time reversal and only term is presented in detail in b or d. The third term/box is time reversal invariant, as presented in c or e. b, c, Cluster expansions of the 4B system into irreducible clusters (represented by the filled or unfilled circles connected by the straight lines) of various orders (sizes). d, e, Analogous to b & c, but directly in the representation of a band structure for ML-MoTe₂ with valleys (K and K') locked to the spin degree of freedom of electrons. The spin-up and spin-down electrons are colored in blue and red, respectively. For brevity, we exclude those 2B clusters with the same charges, such as e-e and h-h, in the figures, but these clusters are included in our theoretical calculations.
**Experimental results**

Figure 2a represents schematically the experimental situation where a strong pump produces an e-h “soup”: a combination of various excitonic complexes or correlated entities of various orders and their corresponding excited states. Figure 2b shows our device structure of a ML-MoTe\(_2\) sandwiched between two hexagonal boron nitride (h-BN) layers. A back gate was used to control the background charge of the ML-MoTe\(_2\) (see Methods S2). The temperature-dependent reflection contrasts of Device #1 are shown in the continuous-wave (CW) case under the charge-neutral condition at \(V_g = -1\) V in Fig. 2c and for the case of p-type doping at \(V_g = -6\) V in Fig. 2d (see Methods S3.1, Extended Data Fig. 2a–2h, and Ref. 29, for an explanation of the data processing). The grey dots represent the measured CW absorption of the material. According to the fittings of the results at 4K, the X peak is spectrally positioned at \(\sim 1.168\) eV at the gate-compensated charge-neutral voltage, \(V_g = -1\) V (Fig. 2c), and the T peak (only the inter-valley spin-singlet species\(^{30-32}\) in ML-MoTe\(_2\) system) appears at \(\sim 1.149\) eV in the doped regime at \(V_g = -6\) V (Fig. 2d). More importantly, there are no additional absorption features below X in the charge-neutral regime without pump (see the low-energy side of X in Fig. 2c). Typically by measuring the CW absorption and PL spectra, we pre-screened the samples for the following pump-probe experiments and selected those without defects or with low levels of defects (see Methods S3.2, Extended Data Fig. 3).
Fig. 2 | Basics of experiment and key observations. a, Illustration of the e-h “soup” generated by the intense pump pulse, showing the possible 2B and 4B states. b, Schematic of the charge-tunable device by the gate voltage, $V_g$. c, d, CW reflection contrasts $(R - R')/R'$ (see Methods S3.1 for definition) at several temperatures under the charge-neutral condition at $V_g = -1$ V (c) and under the p-doping condition at $V_g = -6$ V (d) (Device #1). The solid lines are the results of the Gaussian fittings. e, Differential absorption spectra (see the main text for definition) at different temperatures for the cross-$(\sigma^+ \sigma^+)$ circularly polarized pump-probe configuration at the pump-probe delay time $t \approx 0$ ps at $V_g = -1$ V. Each spectrum for a given temperature was fitted with 6 Gaussian peaks marked by $P_1 - P_6$. The points are experimental values, while the red solid lines are the results of the Gaussian fittings. f, Plots of the fitted central energies of the Gaussian peaks with respect to the temperatures for $P_1 - P_6$ (e) and $T$ (d). The spectral locations of $T$ marked with the green dashed lines in e were obtained from the CW results in d.

The ultrafast pump-probe experiment is described in Methods S3.3, with the experimental setup illustrated in Extended Data Fig. 4. The pump energy of 1.174 eV is $\sim 6$ meV above X with a fluence of $\sim 60 \mu J \cdot \text{cm}^{-2}$ (corresponding to an e-h pair density $n_p$ estimated to be $\sim 3 \times 10^{12} \text{cm}^{-2}$, see Methods S3.4 for the estimate), while the probe energy was tuned from 1.127 to 1.161 eV with a resolution of $\sim 0.2$ meV. The gate
voltage was set at $-1 \text{ V}$ to maintain charge neutrality. The temperature-dependent transient differential absorption spectra of Device #1 are shown in Fig. 2e. Here, the transient differential absorption ($-\Delta \alpha$) is defined as $-\Delta \alpha \propto -(\alpha_p - \alpha_0) \propto R_p - R_0$, where $R_p$ and $R_0$ are the reflection signals from the sample with and without pump ($\alpha$ denotes the corresponding absorption. See Methods S3.3 and Ref. 33 for the explanation of the relation between the differential absorption and the differential reflection). It is worth noting that $-\Delta \alpha < 0$ means a pump-induced absorption increase, typically related to those of excited-state absorption (ESA) processes. In Fig. 2e, we observe rich spectral features with absorption increases as marked with $P_1 - P_6$. Based on their relative positions to $T$ and $X$, these features and the associated fitted peaks can be divided into three energy intervals: $P_1$, $P_2$ (below $T$), $P_3$, $P_4$ (near but below $T$), and $P_5$ & $P_6$ (above $T$ or between $T$ and $X$). To show the reproducibility of the results (for Device #1), we measured the differential absorption spectrum (the 4K case in Fig. 2e) with a finer spectral resolution of 0.1 meV, as shown in Methods S4, Extended Data Fig. 5.

To obtain more quantitative information about these features, we performed multi-peak Gaussian fittings on the spectra at various temperatures in Fig. 2e (see Methods S5 for the fitting method). The central energies of the obtained Gaussian peaks $P_1 - P_6$ (Fig. 2e) and the fitted peak $T$ (Fig. 2d) are plotted in Fig. 2f versus temperature. The intervals between the neighboring peaks in $P_1 - P_6$ are in the range of 4 – 7 meV, while the total spread of these peaks is around 25 meV. The lowest peak ($P_1$, $\sim 1.134 \text{ eV}$ at 4K) is about 35 meV below the original $X$ peak ($\sim 1.168 \text{ eV}$ at 4K) and $\sim 15$ meV below the $T$ peak ($\sim 1.149 \text{ eV}$ at 4K). When temperature increases from 4K to 80K, $P_1 - P_6$ in the ultrafast spectroscopy (Fig. 2e) show a redshift of $\sim 1 - 3 \text{ meV}$, while peaks $T$ and $X$ extracted from the CW results (Fig. 2c & 2d) show a redshift of $\sim 7 \text{ meV}$. As can be seen in Fig. 2e, $P_1 - P_6$ are well resolved at 4K, but merged more together with increase in temperature due to increased broadening with temperature.
**Fig. 3 | Gate-voltage dependence of the transient absorption.** a, CW reflection contrast contour in the plane of photon energy and gate voltage (Device #2 at 4K). b – k, Differential absorption contours in the plane of probe energy and delay time for the cross- (σ– σ+) (b – f) and co- (σ+ σ+) (g – k) circularly polarized pump-probe configurations. The voltages (5 V, 1 V, –3 V (charge-neutral), –7 V, –11 V) applied for observing the transient differential absorptions in b – k are marked with the five cyan dashed lines in a. In d & i, the similar new spectral features (P₁ – P₆) to those in Fig. 2e are marked accordingly.

We notice that previous studies have also observed a peak below T attributed to charged bi-excitons²⁰–²⁴. To examine the charge dependence of our new spectral peaks, we performed a gate-dependent experiment on a device of the same design (Device #2) at 4K. The gate-dependent CW reflection contrast (or absorption) map is shown in Fig. 3a. Similar to the case of Device #1 (Fig. 2c), there are no observable features below X in the charge-neutral regime (V₈ = –3 V) without pump. A few selected transient differential absorption spectra are shown in Fig. 3b – 3k. From top to bottom, the system was gated into the charge-negative, neutral, and positive regimes corresponding to the five voltages as marked by the cyan dashed lines in Fig. 3a. In Fig. 3b – 3k, the spectral features of P₁ – P₆ similar to those in Fig. 2e are visible, and are the strongest in the charge-neutral situations of V₈ = –3 V (Fig. 3d & 3i). The spectral features are stronger for the case of (σ– σ+) (Fig. 3d) than for the case of (σ+ σ+) (Fig. 3i) (see Methods S4, Extended Data Fig. 5 (Device #1) and Methods S5, Extended Data Fig. 6 (Device #4) for the similar polarization contrast). The contrast between cross- (σ– σ+) and co- (σ+ σ+) polarized cases is also observed for those bi-exciton signals in
previous experiments\textsuperscript{18,19}. It indicates the inter-valley configuration is always more favorable than the intra-valley one\textsuperscript{18,19}. Such a polarization contrast is also reflected in our theoretical results (see Methods S11.1, Extended Data Fig. 14). This situation is also similar to the case of bounding and anti-bounding states of a Hydrogen molecule.

In Fig. 3b – 3k, the features fade away as the system deviates from charge neutrality. Such gate-dependent behavior was also observed for another device of the same design (Device #5) (see Methods S6, Extended Data Fig. 9). Contrary to the previous observations of charged bi-excitons\textsuperscript{20-24} that are the weakest in the charge-neutral regimes, our new peaks $P_1 - P_6$ are the strongest in these regimes, pointing to the existence of charge-neutral entities. In addition to the spectral features of $P_1 - P_6$, we see also an increased absorption ($-\Delta \alpha < 0$) in the vicinity of $X$ in both Fig. 3k & 3i, which is related to the pump-induced bandgap renormalization (BGR)\textsuperscript{34}. A full BGR signal can be seen as the negative ($-\Delta \alpha < 0$, red regions) and positive ($-\Delta \alpha > 0$, blue regions) bands around $X$ (see Methods S5, Extended Data Fig. 6a, 6b, & 6d (Device #4) for such an antisymmetric line-shape around $X$). Compared to $P_1 - P_6$, the BGR signals around $X$ show less the polarization contrast.
**Fig. 4 | Pump-density dependence of the transient absorption.** a, Differential absorption contours in the plane of probe energy and delay time for the cross- (σ− σ+) circularly polarized pump-probe configuration (Device #3, at 4K, measured in the charge-neutral regime). b, Gaussian fittings (red solid lines) of the differential absorption spectra extracted from a (dots) at a delay time of ~ 0.9 ps. Each spectrum is fitted with 6 Gaussian peaks marked by P₁ – P₆ as in Fig. 2e. The spectral location of T is marked with the green dashed lines in a & b. The total e-h pair density, nₚ, generated by the pump was marked in each panel of a & b. c, d, The total areas (corresponding to absorption increment) (c) and central energies (d) of P₁ – P₆ with respect to the above pump densities.

To study the pump-density dependence of P₁ – P₆, we performed a series of pump-probe experiments with a varying pump fluence on a device of the same design (Device #3) at 4K. Based on the results of Device #2 presented in Fig. 3, the system was gated into the charge-neutral regime to have the maximum effects of the spectral features. The pump-fluence-dependent transient differential absorption spectra are shown in Fig. 4a. From top to bottom, the pump fluence was varied from ~ 4 μJ·cm⁻² to ~ 320 μJ·cm⁻² (nₚ estimated to be 2.0×10¹¹ cm⁻² to 1.6×10¹³ cm⁻², see Methods S3.4 for the estimates). Figure 4b show the spectra in x-y plot (corresponding to those of Fig. 4a at the delay time of ~ 0.9 ps) with the multi-Gaussian fittings similar to those shown in Fig. 2e. The integrated intensities and central energies of the fitted Gaussians are plotted in Fig. 4c & 4d, respectively (see Extended Data Fig. 10 for Fig. 4c plotted in a
linear scale). As can be seen in Fig. 4a & 4b, the spectrum is nearly featureless when the pump density is below $4.0 \times 10^{11}$ cm$^{-2}$. As the pump density is above $4.0 \times 10^{11}$ cm$^{-2}$, $P_6$ (between $T$ and $X$) is the first to appear in the spectrum, followed by $P_2 - P_4$ (below or near $T$) & $P_5$ (between $T$ and $X$) with blurred features. With the further increase of the pump density beyond $1.6 \times 10^{12}$ cm$^{-2}$, $P_2 - P_4$ & $P_5$ become increasingly visible and better distinguishable, and $P_1$ (below $T$) starts to appear (better visible in Fig. 4b than in Fig. 4a). When the pump density reaches $8.0 \times 10^{12}$ cm$^{-2}$, all the peaks of $P_1 - P_6$ are visible and can be fitted within relatively small errors (Fig. 4c & 4d). At any pump level as shown in Fig. 4c, $P_1$ is always the weakest among the 6 peaks while $P_6$ is the strongest. The pump dependence described here will be further explained in connection with the discussions of Fig. 5. With the increase of the pump density, $P_1$, $P_2$, & $P_6$ exhibit larger redshifts of ~ 2.5, 2.2, and 2.8 meV than $P_3 - P_5$ of ~ 1.5 meV or smaller (Fig. 4d).

It is known that defects$^{15-17,20,23}$, phonons$^{35-38}$ (i.e. near-exciton resonant Raman scatterings, or exciton phonon replicas, etc), and non-linear mixing effects could sometimes cause additional spectral responses. But those effects can be ruled out as possible origins of $P_1 - P_6$, as explained in the following:

1) Defects: There are possibly two types of absorption associated with defects. One is from the crystal ground state to the defect state (0-2B) called ground state absorption (GSA). The other is from the defect exciton states to a defect related higher excited state (2B-Hi), or excited state absorption (ESA). Clearly the GSA process decreases with pump, known as defect exciton bleaching, while the ESA could in principle increase with pump (see Extended Data Fig. 10, for the reverse trends of the absorptions of $P_1 - P_6$ and $X$ with increase in pumping: an increased absorption for $P_1 - P_6$ and a decreased absorption for $X$). The key features of $P_1 - P_6$ we observed show increasing absorption with pump, so the GSA process can be excluded. Since our pre-screened samples have low level of defects (typically $5 \times 10^{10}$ cm$^{-2}$ (Ref. 23) or lower), the ESA process will be quickly saturated. However, we observe increase of absorption
signal up to density levels on the order of $10^{12}$ to $10^{13}$ cm$^{-2}$, much higher than possible defect levels. Therefore, the defect-related ESA processes can be also excluded. In addition, as shown in PL and absorption spectra (Extended Data Fig. 2i, 2j, 3a, & 3b), we did not observe any defects emissions or absorptions for those pre-screened samples. Therefore, defects can be excluded as potential origins of the spectral features of $P_1 - P_6$.

2) Phonon Effects: As shown in Extended Data Fig. 2i, 2j, 3a, & 3b, we did not observe any emission or absorption features related to exciton-phonon replicas (see Ref. 35-38 for typical observations of phonon-assisted excitonic complexes in those W-based materials). In other words, we did not observe phonons assisting those of 0-2B transitions or any excitons dressed by phonons. Naturally, it will be even more difficult to observe phonon effects in those of weaker 2B-$Hi$ processes. Therefore, phonon effects can be excluded as potential origins of the spectral features of $P_1 - P_6$.

3) Any Emission Signals: Since our observed signals show increased absorption ($-\Delta \alpha < 0$) with pump, those emission processes can be excluded. In principle, none of emission signals could be recorded as time-resolved signals by the pump-probe setup based on the lock-in technique (see Methods S13, in connection with Extended Data Fig. 4), usually such time-resolved emission processes have to be measured by a TCSPC setup.

4) Since our experiments were performed with both the pump and probe beams normal to the sample surfaces and the small thickness of the samples of ~ 60 nm (see Methods S2), the phase-matching conditions cannot be met and the non-linear mixing effects can also be excluded.

In Methods S13, we summarized possibilities that could be ruled out as the source of $P_1 - P_6$. To understand the origin of $P_1 - P_6$, we will develop a many-body theory based on the Bethe-Salpeter equation for the 4B case in the following.
Theory for four-body systems of two electrons and two holes

The standard 2-body Bethe-Salpeter equation (2B-BSE) has been extensively applied to excitonic systems39,40 to obtain the Hydrogen-like Rydberg series41 (see Methods S8 – S10.1). The 3B-BSE has also been applied to explain the trion-related features in 2D materials31,32,42. Figure 5a presents the absorption spectrum calculated using the 3B-BSE for ML-MoTe2, where we see clearly only the T peak in its neighborhood. Obviously, such 3B-BSE does not provide an explanation for the features related to P1 – P6. The BX-related spectral features have been calculated theoretically19,28,43-45 to be between T and X. Specifically, the BX resonance of 14.4 meV below X for ML-MoTe2 was calculated to be between T and X by combining the density functional theory with the path-integral Monte Carlo method43. But so far, there has been no experimental observation of the BXs in MoTe2. In addition, our spectral features P1 – P6 contain more spectral peaks in a much larger spectral range than those BX related peaks19,28,44,45. To explain these new features, we developed the 4B-BSE theory that describes the 2e2h system by including all the 4B correlations (see Fig. 1). Details of the theory and the calculation of absorption spectra are presented in Method S10.2–S11.2. Here we show only the key steps. The wavefunctions of the 4B and 2B states, \( |e_ih_1e_2h_2\rangle \) and \( |e_ih_i\rangle \), are expressed in terms of creation and annihilation operators,

\[
|e_ih_1e_2h_2\rangle = \sum_{(v_1, v_2, v_3, v_4)} B^{v_1, v_2, v_3, v_4} \hat{a}_{v_1}^\dagger \hat{a}_{v_2}^\dagger \hat{a}_{v_3} \hat{a}_{v_4} |0\rangle, \tag{1}
\]

\[
|e_ih_i\rangle = \sum_{(v_1, c_i)} A^{v_1, c_i} \hat{a}_{v_1}^\dagger \hat{a}_{c_i} |0\rangle, \tag{2}
\]

where \( v_i \)'s and \( c_i \)'s index the single-particle states including the valence (\( v \)) and conduction (\( c \)) band indices with the momenta. Coefficients \( A^{v_1, c_i} \) and \( B^{v_1, v_2, v_3, v_4} \) are determined by the solutions of the 2B-BSE and 4B-BSE, respectively. The corresponding eigen-energies of the 2B and 4B states can also be solved and denoted by \( \epsilon_{e_ih_i} \) and \( \epsilon_{e_ih_1e_2h_2} \), respectively (see Methods S10.1 & S10.2, respectively; See Methods S12 for the numerical techniques). In this way, dielectric function \( \epsilon \) for each
given $|e_j h_j\rangle$ can be calculated via 

$$
\epsilon \propto \frac{2\pi}{\hbar} \sum_{\alpha} \left| \sum_{|v_i, v_f, i, j=1,2,3,4B|} \langle e_j h_j | \mathbf{e} \cdot \mathbf{p} | e_i h_i e_{v_i} h_{v_f} \rangle \right|^2 \Gamma \left( \epsilon^{\sigma^+}_{v_i, v_f, h_i, h_j} - \epsilon^{\sigma^-}_{v_i, v_f, h_i, h_j} - \hbar \omega - i\gamma \right), \quad (3)
$$

where, $\hbar \omega$ is the photon energy, $\mathbf{e}$ is the unit vector of the in-plane electric field component for a normal incident field, $\mathbf{p}$ is the dipole momentum operator defined via $\mathbf{p} = \sum_{(v_i, v_f)} p^{v_i, v_f} \hat{a}_{v_i} \hat{a}_{v_f}$ with the independent-particle inter-band dipole momentum $p^{v_i, v_f}$ given in Methods S8 (see eq. (S8) & (S9)), $\alpha$ is the serial number of all the 4B eigen-states in the sequence of the eigen-energies from low to high, and $\Gamma$ represents the Gaussian broadening function with a phenomenological broadening parameter, $\gamma$. Finally, the absorption coefficient is given by the imaginary part of the dielectric function for both ($\sigma^- \sigma^+$) and ($\sigma^+ \sigma^+$) pump-probe configurations.

Clearly, one has to calculate the dipole matrix elements of all the 2B-4B transitions to obtain the dielectric function (eq. (3)). Even more challenging is the knowledge of the distributions and weightings of all the possible species in the “soup” at a given set of parameters (temperatures and the total $e$ or $h$ densities, etc.). In the case of $e$-$h$ 2B systems such as excitons and plasmas, a self-consistent description of the coupling between distributions and polarizations is given by the Semiconductor Bloch equation. Since a complete theory involving self-consistent coupling between distributions of all the species in a $2e2h$ 4B system and the possible polarizations is lacking, we will only consider possible spectral contributions from all the $2B$-$4B$ transitions, without considering the exact distributions of various entities and the weighting of each transition.

Another important notice to make of is the relationship between the cluster expansion approach and direct solutions of the 4B-BSE using the Feynman diagrammatic technique. The relations between the terms in these two expansion techniques are given in Methods S10.3. Due to the intuitive pictures and transparent physics of the
cluster expansion approach, we will use the language of cluster expansion to describe the results. For the 2B states, we have a total of 15 discrete states from 1s-X, 2p-X, 2s-X, ... plasma for ML-MoTe$_2$ (see Methods S10.1). For the 4B states, we consider following three cases of truncation (see Methods S1, Extended Data Fig. 1), in order to extract and identify the effects of each: Case 1, up to △ △; Case 2, up to △ △; Case 3, up to △ (see Methods S10.2 – S11.2). For each case, a series of 4B states are solved from the corresponding truncated 4B-BSE. The dipole matrix elements of all the possible 2B-4B transitions are then calculated as follows,

$$\langle e_3, e_1 | \hat{p} | e_4, e_2, h_2 \rangle = \sum_{(v_i, e_i, j=1, 2, 3, 4)} (A^{v_i, e_i})^* B^{v_i, e_i, e_j} p^{v_i, e_i} \langle 0 | \hat{a}_{v_i}^\dagger \hat{a}_{e_i}^\dagger \hat{a}_{e_j} \hat{a}_{e_i} \hat{a}_{e_j} \hat{a}_{v_i} \hat{a}_{v_j} | 0 \rangle. \quad (4)$$

An expansive form of eq. (4) can be seen in Methods S11 (eq. (S19)). The dipole matrix elements thus calculated are inserted into eq. (3) (see also eq. (S20)) to obtain the spectra corresponding to photon absorption or emission shown in Fig. 5b – 5e (see also Extended Data Fig. 14 & 16).

To obtain a correct and complete picture of the possible 2B-4B transitions, especially the relative positions of spectral lines and their origins, we emphasize here the difference between the typical optical spectrum and the total-energy spectrum. Such total-energy spectrum of the 2e2h 4B system is shown in Fig. 5g (see Extended Data Fig. 16 for the 4B system restricted to △ △, △ △ and △). It is important to realize that the optical spectrum measured in an absorption or emission experiment does not reflect the absolute energies on the total energy scale. As shown in Fig. 5g (see also Extended Data Fig. 16), a series of transitions occur between different 2B states and the corresponding 4B states on the total energy scale, as marked by the vertical double-arrowed lines with ① – ⑥ (6 examples, selected out of 15 2B states shown in Extended Data Fig. 16). The actual spectrum of the transitions corresponding to the superposition (Fig. 5j) of all possible individual transitions at different total energies are shown schematically in Fig. 5g. Unfortunately, such total-energy spectra
are not easy to obtain in an optical experiment, where only the energy difference (photon energy) between the initial and final states of these transitions is measured. Or equivalently, all these total energy spectra are shifted relative to a common reference (e.g. the 1s-X energy), as shown in Fig. 5i. The actual optical spectrum is the superposition (Fig. 5j) of 15 of these spectra shown in Fig. 5i, or 15 vertically “collapsed” spectra shown in Fig. 5h (see also the same layout for each figure in Extended Data Fig. 16).
**Fig. 5 | Theory-experiment comparison of absorption spectra.** a–e, Absorption spectra calculated based on the 3B-BSE (a) and the 4B-BSE (b–e) for ML-MoTe$_2$. d shows the spectra of transition between the 2B state (1s-X) and the 4B states solved from the full 4B-BSE. b, c, & e show the cases with the same 2B state (plasma), but the 4B states solved from the 4B-BSE truncated up to $\triangle \triangle$ (b), $\triangle \triangle$ (c), and $\triangle$ (e). The vertical dashed line is the calculated trion (T) energy. The vertical black lines underneath the spectral profiles mark the calculated spectral positions with the height representing the strength of the dipole transitions calculated from eq. (3) (see also eq. (S19)). The spectral function, $\Gamma$, in eq. (3) is a Gaussian with a broadening parameter, $\gamma$, chosen to be 0.5 meV (unfilled profiles) or 2 meV (shaded profiles). We label the Gaussian-broadened peaks in each spectrum with italic numerals from low to high energy. The solid black profile in f represents differential absorption spectrum, $\Delta \alpha$, at the zero delay for Device #2 at 4K in the charge-neutral regime, where we also overlay the contour of $-\Delta \alpha$ in the plane of probe energy and delay time (see also Fig. 3d). The features are labelled with $P_1$ – $P_6$ (and X), consistent with those in Fig. 3d. The relationship between the total-energy spectra and the optical spectra is shown in g–j (see the main text for details). The calculated total energies are shown beside the upward axis in g for those typical 2B and 4B states (not to the scale, see Extended Data Fig. 15 for such a total-energy spectrum and the optical spectra plotted strictly to energy scale). The energy range of 1.432 – 1.770 represents the continuous absorption band (see Methods S10.1). Transition ① and ⑥ correspond to d & e, respectively. The flag notation in g marks the 4B ground state, whose spectral feature corresponds to peak J in d.
Figure 5b & 5c show the optical spectra corresponding to $\langle e_3h_3|\hat{p}|e_ih_1h_2\rangle$ in eq. (4) with the 4B states calculated from the 4B-BSE truncated up to $\triangle\triangle$ (Fig. 5b) and $\triangle\triangle$ (Fig. 5c) and the 2B state given the plasma state (see transition 6 in Extended Data Fig. 16a & 16b, respectively). We notice a peak between T and X in the case of $\triangle\triangle$ (peak 1 in Fig. 5c) versus the featureless background in $\triangle\triangle$ (Fig. 5b). Strictly speaking, the only peak in Fig. 5b represents a 4B state of non-interacting (1s-X)(plasma) (without wavy lines). In the case of Fig. 5c, $\triangle\triangle$ introduces interaction (wavy lines) between the low-order clusters, leading to the formation of $\triangle\sim\triangle\triangle$, or (1s-X)~(plasma) (see Methods S1, Extended Data Fig. 1e). Therefore, peak 1 and the tiny splitting peaks below X in Fig. 5c should correspond to those of $\triangle\triangle$ or $\triangle\sim\triangle\triangle$. Clearly, we do not see any spectral features corresponding to P1 – P4, especially the features below T. This means that P1 – P4 do not originate from cluster $\triangle\triangle$ or $\triangle\triangle$.

Our next approximation is to include all the 4B states calculated from the full 4B-BSE (truncated up to $\triangle\triangle$). The relationship between the total-energy spectra and the optical spectra in this case is shown in Fig. 5g – 5j (see also Extended Data Fig. 16c). The optical spectra calculated with the 2B states given the 1s-X (transition 1) and plasma (transition 6) are shown in Fig. 5d & 5e, respectively (see Methods S12, Extended Data Fig. 18 & 19, for the convergence test of the spectra in Fig. 5c – 5e). A direct comparison is shown in Fig. 5f and Extended Data Fig. 14c & 14f (It is very important to point out that the experimental result should not be compared with only one of these calculated spectra, because the actual spectrum is a superposition of all possible 2B-4B transition spectra as we illustrated in Fig. 5g and Extended Data Fig. 17c). We see that the spectral features (peak 1 – 6 in Fig. 5e, and those in Extended
Data Fig. 16c & 17c) in the entire spectral region resemble closely to those of \( P_1 - P_6 \). In other words, the spectral features of \( P_1 - P_4 \) originate from cluster \( \Delta \). By comparing various 2B-4B transitions in Fig. 5g – 5j for cluster \( \Delta \) (see also Extended Data Fig. 16c & 17c), clusters \( \Delta \Delta \) (see Extended Data Fig. 16b & 17b), and \( \Delta \Delta \) (see Extended Data Fig. 16a & 17a) both on the total-energy scale and optical spectrum, we notice that the following: The states from cluster \( \Delta \) for each of the same 2B states have lower energies and are thus more stable than those of \( \Delta \sim \Delta \) (BX) and \( \Delta \sim \Delta \) (T\( \sim \)e and T\( \sim \)h), indicating the most stable existence of cluster \( \Delta \) or quadruplon. Importantly, we notice from the transitions in the total-energy scale that the lower-frequency features (below T) in the optical spectrum such as \( P_1 - P_3 \) correspond to the transitions (such as 4, 5, and 6 in Fig. 5g) between the more-excited states in the 4B manifold. This explains why \( P_1 - P_3 \) decays faster as we mentioned in connection with the discussions of Extended Data Fig. 6a & 6d for Device #4. Nearly all the 2B-4B transitions shown in the total-energy spectrum in Fig. 5g, e.g. from 1 (low energy) to 6 (high energy), can contribute to the spectral peaks between T and X. Especially, the spectral peak related to the 4B ground state is calculated to be between T and X (close to \( P_5 \) or \( P_6 \), see the flag notation in Fig. 5d). This explains why \( P_6 \) has the largest intensity and appears the earliest with increasing pump (Fig. 4). However, only the transitions between the highly excited 2B and 4B states such as those of 3 – 6 in Fig. 5g, can contribute to the peaks well below T. The fact that \( P_1 \) only emerges at high pump levels signifies the existence of highly excited states of both the 2B & 4B entities. Through such 2B-4B spectroscopy, we observe a much more complex many-body system with more refined interplays of these 2B, 3B, and 4B complexes than the simple picture of the Mott transition. The similar spectra (such as Fig. 5d & 5e) were also calculated for the inter- (\( \sigma^- \sigma^+ \)) and intra- (\( \sigma^+ \sigma^+ \)) valley 4B states (Extended Data Fig. 14), and extensively discussed in connection with such continuous Mott transition (see Methods S11.1).
It is important to note that $\triangle$ in the 4B cluster expansion represents a $2e2h$ 4B irreducible cluster, where none of the 2 electrons or 2 holes belongs to a specific exciton, or there is no a well-defined exciton in such a 4B system. The entity is therefore not a bi-exciton or an excited-state bi-exciton anymore, rather a quadruplon, as schematically shown as the last cluster in Fig. 1b – 1e. We notice that exactly such a system was recently calculated for a quantum dot system and was called a “quadron”\(^2\). Therefore, our consistent theoretical and experimental results show that the spectral features corresponding to $P_1 – P_4$ indeed originate from the quadruplons. Similar quadruplon consisting of 4 identical fermions was recently theoretically studied in a 1D Hubbard model\(^1\).

**Conclusion**

The focus of this paper is the experimental observation of several new spectral peaks that appeared below the trion features and the development of a microscopic theory based on the 4B-BSE to explain the origin of these peaks. The observation of these peaks covering a large energy range of $\sim 40$ meV was made experimentally possible through a helicity-resolved pump-probe spectroscopy in gate-controlled ML-TMDC samples. Through the establishment of a systematic relationship between the Feynman diagrams of the 4B-BSE and cluster expansions of various orders, we showed that these new spectral features could not be explained by clusters associated with trions or bi-excitons, while the irreducible cluster associated with $2e2h$ was necessary and sufficient in producing these new spectral features. This agreement between our new theory and experiment established the existence of a new correlated 4B entity, the quadruplon. The existence of the 4B entity is further corroborated by the pump dependent experiment where systematic changes of the absorption spectra are consistent with the possible occupation of higher 2B states and the existence of the final 4B states upon the absorption of the probe photons. Interestingly, these 4B states can stably exist even at a relative high temperature of $\sim 60$ K.
The field of many-body physics involving high order correlations has been quite active recently. There have been many reports on experimental observations of the possible few-body entities. Suris tetron was experimentally observed recently that contains a conventional exciton and another e-h pair formed near the Fermi surface. However, it is an entirely open question whether the Suris tetron corresponds to a quadruplon-like, a trion-hole-like or a bi-exciton-like entity. Other examples include the quarternion (an exciton bound to two free charges of the same sign), charged bi-exciton or trion-exciton, and even 6B and 8B ones: the hexciton and oxciton (an exciton plus multiple fermi-sea e-h pair, also known as the sub-terms of the exciton polaron together with the Suris tetron), or tri-exciton and quad-exciton, etc. All these many-body complexes are regarded reducible to product states of excitons, trions, and charges, but not systematically discussed in terms of cluster expansion. Thus the possibility of 4B irreducible clusters has not been an issue for these experimental studies. In the context of ultracold gas, the 4B states (related to the Efimov effects) were theoretically discussed in terms of all irreducible clusters such as $B_4$, $B_3+B$, $B_2+B+B$, $B_2+B_2$, or $B+B+B+B$. Attempts were also made to explain an earlier experiment in terms of the above theory. Also, the quadruplons consisting of 4 holes were theoretically revealed in the sequence of Q (quadruplon), T (triplon), D (Doublon), and B (Band-like part) in the calculated two-hole excitation spectrum at different filling factors in a 1D Hubbard model.

To conclude, the observation of quadruplons would also contribute in a very important way to the fundamental understanding of the Mott transition, one of the most celebrated aspects of condensed matter physics. The existence of a new 4B entity adds to the complexity of the Mott physics and would definitely lead to more new physical phenomena. For example, the co-existence and mutual conversion of various known species have been the subjects of extensive studies for their interesting optical transitions, leading to bi-exciton gain or trion gain. Bi-exciton emission processes are also related to the generation of entangled photons. It would be of great interests
to study the co-existence and mutual conversion of quadruplons with other known species. The existence of quadruplons opens many new exciting opportunities to study its consequences on optical gain, generation of quantum states, and nonlinear optics, beyond the Mott transitions.

Finally, our study may stimulate more similar studies to search for clusters or many-body complexes of even higher orders beyond the quadruplons and their excited states. Another interesting issue that arises from this study is the experimental study of the total energy spectrum of a $2e2h$ 4B system. As shown in Fig. 5g, the total energy of the $2e2h$ system extending over $\sim 0.3 - 0.6$ eV shows very rich spectral features that cannot be determined through optical spectroscopy. A comparison of our 4B-BSE theory with the total energy spectrum would allow us to study many different states of the 4B irreducible clusters in a more unique fashion. More importantly, it would allow the determination of the relative energetic stabilities of various states. Among all of these states, the experimental verification of the relative stability of bi-excitons versus quadruplons would be of great special interest.

Data availability
The data that support the findings of this study are available from the corresponding author upon request.

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Author Contributions
J.T. and Q.Z. prepared the materials and fabricated the devices with help of Z.W. for the metal electrodes. X.D. and H.S. built the pump-probe optical setup. H.S., X.D., J.T., and Q.Z. optimized the optical system and automated the data acquisition. J.T. and Q.Z. conducted the optical experiments and measurements. J.T. processed the data under guidance of C.Z.N. and H.S.. J.T. developed the many-body theory and performed the theoretical modelling and calculations under guidance of C.Z.N.. C.Z.N. made the initial connections with the irreducible cluster expansion model and the quadruplons, while J.T. and C.Z.N. eventually worked to establish these connections. J.T. and C.Z.N. performed the data analysis and wrote the manuscript with inputs from H.S. at the initial stage. C.Z.N. supervised the overall project.

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The authors declare no competing interests.

Extended data figures and tables