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Many-body quantum physics in XANES of highly correlated materials, mixed-valence oxides and high-temperature superconductors

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Many-body final states in X-ray absorption near-edge structure (XANES) using synchrotron radiation are a unique tool for probing quantum many-body initial states in complex electronic correlated systems where single-particle descriptions of electronic states in a periodic potential break down. Multi-electron excitations were first observed in the 1960s in X-ray absorption spectra of atoms and subsequently in molecules and complex solids. The applications of XANES many-body final states to probe unique features of electronic correlation in heavy fermions, mixed-valence systems, mixed-valence oxides and high-temperature superconductors are discussed.

1. Historical introduction to many-body effects in physics: from atomic physics to condensed matter

The origin of many-body quantum physics is usually associated with the publication by Heisenberg in 1926 of the paper in which he provided a theoretical interpretation of the energy splitting of the spectral lines, called orthohelium and parahelium, in helium atomic gas absorption spectra (Heisenberg, 1926). In this work, Heisenberg assumed that the motion of the two electrons in helium is correlated, considering it as the simplest many-body electronic system, made up of only two electrons. Therefore, he described a quantum resonance between two electronic configurations of the two electrons. In this work, he introduced the exchange interaction giving the energy splitting between symmetric and antisymmetric wavefunctions. Following the article on the Fermi statistics for the electron gas in metals (Fermi, 1926), Dirac introduced the distinction of Fermi versus Bose statistics for fermions versus bosons characterized by an antisymmetric versus a symmetric wavefunction, respectively (Dirac, 1926). The exchange interaction between bosons is attractive, giving a quantum Bose condensate at $T = 0$, while the exchange interaction is repulsive for fermions, giving a degenerate Fermi gas at $T = 0$. In 1927, Wentzel proposed a nontrivial extension of the Heisenberg theory to explain the nonradiative Auger effect (Wentzel, 1927).

Majorana (1931) extended the Wentzel theory, focusing on the selection rules for the nonradiative decay of two-electron excitations observed in atomic absorption spectra (Foote *et al.*, 1925; Shenstone, 1931). Following the experiment of Beutler on vacuum ultraviolet absorption spectra of rare gases (Beutler, 1935), in which he observed broad lines due to multi-electron excitations appearing beyond the ionization

Related chapters

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potential, in 1935 Fano developed the theory of configuration interaction between discrete and continuum channels (Fano, 1935) with the prediction of the asymmetric line-shape of the absorption spectrum of two-electron excitations.

The Fano theory was tested by the experimental line-shape of shape resonances in nuclear scattering experiments due to configuration interaction between open and closed scattering channels (Blatt & Weisskopf, 1952; Blatt *et al.*, 1953; Feshbach *et al.*, 1954).

The Fano theory was extended to many different scattering channels in many-body systems by Feshbach (1958). Today, the Fano–Feshbach resonances are of high scientific interest in many different fields, and in particular for ultracold gases and high- T_c superconductivity (Vittorini-Orgeas & Bianconi, 2009).

In 1958, Fano proposed the development of synchrotron-radiation research to measure the high-resolution soft X-ray absorption spectra of atoms using the 180 MeV synchrotron at the National Bureau of Standards (NBS) in the USA and the 1 GeV synchrotron at Frascati in Italy. He proposed to investigate the line-shape of two-electron excitations in rare gases and published a second extended version of his 1935 paper in *Physical Review* (Fano, 1961). The experiments at NBS (Madden & Codling, 1963, 1965) provided a clear experimental confirmation of the asymmetric Fano line-shape for two-electron excitations in helium, neon and argon, where the interference of a discrete auto-ionized state with a continuum gives rise to characteristically asymmetric peaks in soft X-ray absorption spectra (Cooper *et al.*, 1963).

The Fano–Feshbach resonance in many-body configuration interaction between discrete and continuum states is a fundamental quantum process that was first observed in X-ray absorption spectra but was soon applied in condensed matter physics to describe magnetic impurities embedded in a metallic host, in the so-called Anderson impurity model (Anderson, 1961), and in the prediction of the characteristic change in electrical resistivity with temperature known as the Kondo effect (Kondo, 1964), which is due to the scattering of conduction electrons by magnetic impurities. Today, it is very popular in a variety of systems ranging from heavy fermions to Kondo insulators.

In the period 1969–1975 synchrotron-radiation research was carried out at small synchrotrons at Madison in the USA and Tokyo in Japan and at large synchrotrons in Hamburg in Germany and Frascati in Italy, and scientific interest shifted from atomic physics to condensed matter. Many-body theories predicted many-body final-state effects at the absorption threshold of metals in the soft X-ray absorption spectra (Roulet *et al.*, 1969; Nozières & De Dominicis, 1969; Schotte & Schotte, 1969; Mahan, 1971; Hedin *et al.*, 1970; Combescot & Nozières, 1971). Similar many-body effects predicted in X-ray photoelectron spectroscopy (XPS; Doniach & Sunjic, 1970) for metals were supported by measurements of the asymmetric line-shape of core-level spectra (Antonangeli *et al.*, 1977).

Investigations of two-electron excitations were extended to different excitations at high energies in helium (Dhez &

Ederer, 1973) and in krypton (Bernieri & Burattini, 1987). Two-electron excitations were subsequently found in solids, for example in solid neon (Soldatov *et al.*, 1993), in vanadium, chromium and manganese $3d^0$ compounds with tetrahedral coordination (Bianconi, Garcia *et al.*, 1991), in SiCl_3 and SiF_3 (Di Cicco *et al.*, 1992), in hydrated calcium (D'Angelo *et al.*, 2004) and in rare-earth alloys (Chaboy *et al.*, 1990, 1994).

Many-body final-state effects related to core-hole excitation have been observed in the X-ray absorption spectra of palladium hydrides (Benfatto *et al.*, 1983), and many-body plasmon excitations have been shown to play a relevant role in the photoemission cross section near the C K -shell threshold (Bachrach & Bianconi, 1982). However, the many-body effects in X-ray absorption spectra of metals give only subtle changes in the line-shape of the absorption threshold which are difficult to observe.

2. Many-body effects in XANES: shape resonances in molecules and condensed matter

The interest of the scientific community has mainly been focused on understanding one-electron final-state effects owing to the role of density of states (DOS) in the conduction band, as shown, for example, in the edge region of the $L_{2,3}$ absorption spectrum of aluminium (Balzarotti, Bianconi & Burattini, 1974) measured in the Solidi Roma facility at the 1 GeV synchrotron in Frascati, Italy. Synchrotron-radiation spectroscopy using high energy and large accelerators (3.5 GeV at SPEAR in Stanford and 7.4 GeV at DESY in Hamburg) focused on the weak features in the high-energy range known as Kronig structure, which were renamed with a new acronym, EXAFS (extended X-ray absorption fine structure). The theory of, and experiments on, weak EXAFS oscillation in a variety of complex systems evolved rapidly from 1970 to 1980. In contrast, the theoretical interpretation of the low-energy part of the X-ray absorption spectra giving strong absorption peaks in the continuum of solids, both crystals and glasses, assigned these features to shape resonances (Balzarotti, Bianconi, Burattini *et al.*, 1974), while previously these peaks were qualitatively assigned to transitions to unoccupied DOS of the crystal or atomic final states. The physics was clarified by the observation of the shape resonance in the continuum of K -edge absorption of the nitrogen molecule (Bianconi, Petersen *et al.*, 1978).

The shape resonance is a short-lived final state made of a quasi-stationary state formed by a multiple-scattering resonance of the photoelectron, degenerate with the continuum. Its spatial localization in a nanoscale cluster is determined by the high scattering amplitude of the low kinetic energy, 10–50 eV, of the photoelectron from neighbouring atoms. The very short lifetime of the final state is of the order of 10^{-15} s, which is determined by the core-hole lifetime and decay time of the shape resonance into the continuum. The shape resonances are related to the effects of electronic correlation in molecules (Langhoff & Davidson, 1974; Broad & Reinhardt, 1976; Dehmer & Dill, 1975, 1976; Dehmer *et al.*, 1979; Loomba

et al., 1981). In a set of papers (Bianconi, Doniach *et al.*, 1978; Bianconi, 1979, 1980) the acronym XANES (X-ray absorption near-edge structure) was coined to indicate the spectral features in the absorption spectra of condensed matter, including biological systems, chemical compounds, liquids, amorphous systems and glasses, due to shape resonances for the photoelectron, which in the final state is confined for a short time in a nanoscale cluster centred on the selected atom. The XANES energy range, which extends 50–100 eV beyond the absorption edge, is defined as that where the photoelectron wavelength is larger than the interatomic distance. Here, the full multiple-scattering theory is needed to predict the observed multiple-scattering resonances, and it was shown that the XANES variation due to subtle structural changes in iron(II) and iron(III) hexacyanide complexes can be predicted and understood (Bianconi, Dell'Arriccia *et al.*, 1982).

Today, XANES data analysis (Della Longa *et al.*, 1995) using the full multiple-scattering theory provides the coordination geometry and higher order structural correlation function in the liquid phase (Garcia, Benfatto *et al.*, 1986; Garcia, Bianconi *et al.*, 1986) and in a large variety of disordered systems.

3. Applications to strongly correlated materials

The search for many-body final states in XANES focused on valence-fluctuating materials such as ytterbium intermetallics (Rao *et al.*, 1980), TmSe (Launois *et al.*, 1980; Bianconi, Modesti *et al.*, 1981) and CePd₃ (Sarode *et al.*, 1981), where it was shown that the quantitative mixed-valence state could be extracted from the data.

After the discovery of superconductivity in the first heavy fermion system CeCu₂Si₂ (Steglich *et al.*, 1979), several groups started to look for experimental evidence of strong electronic correlation in intermetallics. Heavy fermions are at the edge between superconductivity and magnetism. In heavy fermions at the chemical potential a narrow *f* band, with a large effective mass, coexists with a wide *d* band (Jarlborg *et al.*, 1983). These materials show strong Pauli paramagnetism and electronic complexity (Lieke *et al.*, 1982), and their electronic properties emerge from multi-electron electronic configurations. A breakdown of the single-electron approximation in the XANES of heavy fermions such as CeCu₂Si₂ (Bianconi, Campagna *et al.*, 1981) and EuPd₂Si₂ (Nagarajan *et al.*, 1981) has been found and evidence for the competition between two many-body electronic configurations was clearly detected by XANES.

The intermediate valence probed by core-level spectroscopy has been investigated in light (cerium) versus heavy (thulium) rare earths. Unique information on electronic correlation, localization and local environment effects has been obtained by *L*-edge XANES (Bianconi, Campagna *et al.*, 1982). The changes of many-body electronic configurations at the Fermi level at the phase transition from the α to the γ phase of cerium have been observed at the Ce *L*₃ absorption edge (Lengeler *et al.*, 1983). The effects of dilution and chemical pressure on mixed-valence cerium-based systems

such as CeNi₅ have been studied by Raaen & Parks (1983) and Parks *et al.* (1983). The roles of the localization and mixing of many-body configurations in intermetallic compounds RPd₃ (where *R* = La, Ce, Pr, Nd, Sm) have been measured by Bianconi, Marcelli *et al.* (1984, 1985) and Marcelli *et al.* (1984, 1985) using *L*₃ and *L*₂ XANES spectra. The many-body final states in inner-shell photoemission and photo-absorption spectra of lanthanum and cerium strongly correlated electronic compounds have been interpreted theoretically using the Anderson impurity model (Kotani, Jo *et al.*, 1987; Kotani, Okada *et al.*, 1987).

In the many-body XANES final states, the deep core level removes the degeneracy of many-body electronic configurations in the initial states in correlated electronic systems. This feature was used to probe the variation of many-body electronic configurations at the metal–insulator transition in V₂O₃ (Bianconi & Natoli, 1978) and in VO₂ (Bianconi, 1982) by measuring the high-resolution V *K*-edge absorption spectrum. In 1985 the theory of correlation gaps in the electronic structure of charge-transfer Mott insulators was presented (Zaanen *et al.*, 1985), showing the existence of a different class of Mott insulators involving both the metal and ligand orbitals in some transition-metal compounds. Using the O *K*-edge XANES of NiO, Davoli *et al.* (1986) provided the first direct evidence for the correlation gap between 3*d*⁸ and 3*d*⁹L multi-electron configurations (where L indicates the hole in the ligand orbital), in agreement with the predictions of Zaanen *et al.* (1985). Many-body configurations in the X-ray absorption spectra of charge-transfer gap insulators have been measured in other correlated systems such as nickel dihalides (van der Laan *et al.*, 1986), in agreement with the theory (Zaanen *et al.*, 1986), uranium 5*f* oxides and glasses (Petiau *et al.*, 1986) and 4*f* compounds (Bianconi, Marcelli, Dexpert *et al.*, 1987) such as PrO₂ (Bianconi, Kotani *et al.*, 1988) and Ce(SO₄)₂ (Bianconi *et al.*, 1985). Full information on ground-state many-body configurations of CeO₂, MO₂ (*M* = Ce, Pr, Tb, Hf) and LaF₃ has been obtained by joint Ce *L*₃-edge XANES and deep metal 3*p* core X-ray photoemission spectroscopy (XPS) using hard X-ray spectroscopy of tetravalent oxides (Bianconi, Clozza *et al.*, 1989; Bianconi, Miyahara *et al.*, 1989).

The discovery in 1986 of high-temperature superconductivity in copper oxides triggered great interest in the nature of new metallic states induced by chemical doping of strongly correlated layered copper oxides. The strongly correlated many-body state of the copper oxide plane was studied by Cu *L*_{2,3} XANES (Bianconi, Congiu Castellano, De Santis, Rudolf *et al.*, 1987), by Cu *K*-edge XANES (Bianconi, Congiu Castellano, De Santis, Politis *et al.*, 1987) and by Cu 2*p* X-ray photoelectron spectroscopy (Bianconi, Congiu Castellano, De Santis, Delogu *et al.*, 1987). These experiments provided the first direct measure of the Mott charge-transfer gap between the many-body configurations Cu3*d*⁹–O2*p*¹⁰ (called 3*d*⁹) and Cu3*d*¹⁰–O2*p*⁵ (called 3*d*¹⁰L, where L is the oxygen hole) in the parent compounds, which was measured to be about 2 eV. These systems can be turned from an insulator to a metal by a variable oxygen interstitials content *y*, as in the high-*T*_c superconductor YBa₂Cu₃O_{6+y}. The variation of the

many-body final states in XANES with variable oxygen content provided the first direct experimental evidence that the itinerant $\text{Cu}3d^9L$ (where L is the hole on the oxygen orbital) many-body configuration is created at the Fermi level in the correlation gap by doping (Bianconi, Congiu-Castellano, De Santis, Rudolf *et al.*, 1987; Bianconi, Clozza *et al.*, 1987*a,b*) and these results were presented at the Taniguchi symposium in Kashikojima, Japan on 19–23 October 1987 (Kanamori & Kotani, 1988). In 1988 these results were confirmed by similar findings in other cuprates (Bianconi, Budnick, Chamberland *et al.*, 1988) and in formally trivalent copper compounds (Bianconi, Budnick, Demazeau *et al.*, 1988). Different interpretations of the XANES data in the frame of single-electron approximation have been proposed by some authors (Groni *et al.*, 1987; Nücker *et al.*, 1987). Only one year later the O K -edge absorption spectra (Nücker *et al.*, 1988) were interpreted in terms of many-body electronic configurations $\text{Cu}3d^9L$ induced by doping. However, while the many-body final state observed in Cu L_3 XANES was assigned to $\text{Cu}3d^9L$ states in the Mott gap of charge-transfer insulators (which is now the accepted assignment), other authors initially assigned the many-body $\text{Cu}3d^9L$ states induced by doping to new unoccupied states in the lower Hubbard band.

In 1988, using polarized XANES spectroscopy of single crystals, it was shown that there were two coexisting different many-body configurations: $\text{Cu}3d^9L(b_1)$, where the holes on the oxygen orbital have a fully planar symmetry $L(b_1)$, and $\text{Cu}3d^9L(a_1)$, where the oxygen holes have a partially out-of-plane symmetry $L(a_1)$ (Bianconi, De Santis, Flank *et al.*, 1988; Bianconi, De Santis, Di Cicco *et al.*, 1988, 1989).

The presence of two states with different orbital symmetry is relevant to superconductivity (Flank *et al.*, 1990). The presence of a second electronic component $\text{Cu}3d^9L(a_1)$ has been shown to be associated with the rhombic distortion of the CuO_4 square plane (Seino *et al.*, 1990) related to charge-density wave onset and polaron formation (Bianconi, Missori *et al.*, 1995).

Full multiple-scattering analysis of polarized K -edge (Li *et al.*, 1991; Bianconi, Li *et al.*, 1991) and Cu L_3 -edge (Pompa *et al.*, 1991; Bianconi, Della Longa *et al.*, 1991) XANES of La_2CuO_4 and $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+y}$ have clearly shown that many-body final-states configurations give a splitting of the strongest peak in the Cu K -edge XANES. The presence of two sets of states at the Fermi level with different orbital characters has been confirmed by many experiments at the O $1s$ and Cu $2p$ edges in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$, $(Y,R)\text{Ba}_2\text{Cu}_3\text{O}_7$ (Pellegrin *et al.*, 1993), $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+y}$ (Pellegrin *et al.*, 1995), $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+y}$ (Pellegrin *et al.*, 1996) and $\text{Pr}_x\text{Y}_{1-x}\text{Ba}_2\text{Cu}_3\text{O}_{7-y}$ (Merz *et al.*, 1997). Today, the two electronic many-body components seen by XANES provide the experimental base for the recent development of the theory of multigap superconductivity both in cuprates (Valletta *et al.*, 1997; Bianconi *et al.*, 1997; Perali *et al.*, 2012) and in other high-temperature superconductors, including pressurized sulfurhydrides (Bianconi & Jarlborg, 2015*a,b*; Jarlborg & Bianconi, 2016) and K-doped p -terphenyl (Mazziotti *et al.*, 2017).

4. Many-body effects in the XANES of complex transition-metal oxides

A major advance in the theory of XANES spectra has been achieved in predicting features due to multiple scattering resonances in the single-particle final-state approximation using the finite-difference method, which allows completely free potential shape and is not constrained to the muffin-tin approximation (Joly, 2001), and new computer codes have become available to calculate many-body final states (Rehr *et al.*, 2009), focusing in particular on transition-metal oxides (Calandra *et al.*, 2012).

In particular, great interest has been directed towards Mn K -edge XANES of manganites in order to understand the controversial issue of manganese valence states. The calculated Mn K edge of the simple oxide LaMnO_3 has been shown to be due to the convolution product of the single-electron XANES and the spectrum of many-body excitations in the Mn–O electronic states upon the sudden switching on of the Mn $1s$ core hole (Ignatov *et al.*, 2001). A small feature standing approximately 6 eV above the main absorption peak due to the multiple scattering resonance is beyond the single-electron approximations and is assigned to a many-body final-state configuration, as in the K -edge XANES of cuprates. The XANES of LaMnO_3 has shown that it is a charge-transfer (CT)-type insulator with a substantial O $2p$ component in the ground state, and the controversial issue of disproportionation in manganese valence states has been understood as a mixture of the CT many-body electronic configurations coupled with spin and lattice degrees of freedom (Chaboy, 2009; Vries *et al.*, 2003; García *et al.*, 2010). Finally, the difficulties in obtaining a reliable comparison between experimental XANES spectra and theoretical simulations have shown that the electronic occupation and the local structure fluctuations in colossal magnetoresistance materials cannot be separated either experimentally or theoretically. In this way, the geometrical and electronic structure of the Mn atom in mixed-valence manganites cannot be described as a bimodal distribution of the formal integer Mn^{3+} and Mn^{4+} valence states corresponding to the undoped references. The understanding of manganese valence-fluctuating systems has allowed advances in understanding colossal magnetoresistance materials as a function of doping, such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, in terms of spin-orbital and local lattice fluctuations, which have been confirmed by resonant X-ray scattering (Subías *et al.*, 2007).

5. Many-body configurations in magnetic circular-dichroism and resonant X-ray scattering experiments

The spin–orbit interaction in the conduction band is not predicted for centrosymmetric solids by standard band-structure calculations. Focusing on the asymmetry of the L_3 white line, which is a probe of many-body final states, X-ray magnetic circular dichroism (XMCD) of iron, cobalt and nickel at the $L_{2,3}$ -edge X-ray absorption near-edge structure (XANES) has been calculated using the local spin-density approximation (LSDA) plus dynamical mean-field theory

(DMFT) (Šipr *et al.*, 2011). The anomalous experimental ratios of the intensities of the L_2 and L_3 peaks, which probe spin–orbit interaction in the conduction band, have not been explained. This indicates that more work is needed to obtain more accurate predictions of the $L_{2,3}$ -edge XANES and XMCD spectra.

The valence- and spin-state evolution of manganese and cobalt in the $\text{TbMn}_{1-x}\text{Co}_x\text{O}_3$ series has been determined by means of soft and hard X-ray absorption spectroscopy (XAS) and K X-ray emission spectroscopy (XES). The spectroscopic techniques reveal the occurrence of high-spin (HS) Mn^{4+} and a fluctuating valence-state low-spin (LS) $\text{Co}^{2+}/\text{HS Co}^{3+}$ in this composition range. Disorder and competitive interactions lead to a magnetic glassy behaviour in these samples (Cuartero *et al.*, 2016).

A complex electronic structure made of both localized and delocalized $\text{Ti } 3d$ carriers and distorted Ti^{3+}O_6 octahedra has been found at the 2D metallic interface in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures using resonant inelastic X-ray scattering at the $\text{Ti } 2p_{3/2}$ edge (Zhou *et al.*, 2011).

The metal–insulator transition and the intriguing physical properties of rare-earth perovskite nickelates have been solved by combining X-ray absorption and resonant inelastic X-ray scattering (RIXS) spectroscopies, taking an NdNiO_3 thin film as a representative example. The unusual coexistence of bound and continuum excitations has been observed in the RIXS spectra, showing oxygen holes in the ground state of these materials (Bisogni *et al.*, 2016). Strongly correlated insulators are broadly divided into two classes: Mott–Hubbard insulators, where the insulating gap is driven by the Coulomb repulsion U on the transition-metal cation, and charge-transfer insulators, where the gap is driven by the charge-transfer energy Δ between the cation and the ligand anions. The relative magnitudes of U and Δ determine which class a material belongs to, and subsequently the nature of its low-energy excitations. The doped cuprates are the most popular case of doped charge-transfer insulators. The use of the novel high-resolution inelastic X-ray emission scattering experimental method has stimulated a revival of the investigation of the parent compounds of cuprates, CuGeO_3 , CuO , La_2CuO_4 and SrCuO_2 . The $\text{Cu } L_{2,3}$ and $\text{O } K$ -edge resonances have shown a large spread in the energy-loss values of the RIXS features for different compounds, showing key electronic differences between cuprate families (Duda *et al.*, 2002). The low-dimensional charge-transfer insulator Li_2CuO_2 (Monney *et al.*, 2016) has shown how the elementary lattice, charge, spin and orbital excitations are entangled in this material. This results in a large lattice-driven renormalization which significantly reshapes the fundamental electronic properties of Li_2CuO_2 (Johnston *et al.*, 2016). By means of resonant inelastic X-ray scattering at the $\text{Cu } L_3$ edge, the spin–wave dispersion in the undoped cuprate $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ has been investigated. These new results may enable a quantitative test of predictions of quantum many-body calculations of magnetic excitations and of electronic correlations in cuprates (Lebert *et al.*, 2017). Recently, an *ab initio* computational scheme for the calculation of X-ray absorption and resonant inelastic X-ray scattering

spectra has been proposed to include relaxation and polarization effects due to the inner core hole. Good agreement is found with experimental transition-metal L -edge data for the strongly correlated d^9 cuprate Li_2CuO_2 (Bogdanov *et al.*, 2017).

6. Conclusions

There is now rapid development of new improved-brilliance diffraction-limited storage rings (DLSRs), which will allow the development of experimental methods to investigate many-body configurations in quantum materials. DLSRs will allow increasing energy resolution and signal intensity while simultaneously reducing the sampled spot size to new limits. The spectroscopic techniques of resonant inelastic X-ray scattering (RIXS), which measures the intensities of excitations as a function of energy and momentum transfer (Schmitt *et al.*, 2014), scanning nano-XANES (SNXANES), which probes both many-body electronic configurations and spatial fluctuations (Poccia *et al.*, 2014), and scanning nano X-ray diffraction (SNXRD), which probes both the k -space and real-space fluctuations (Campi *et al.*, 2015), in a broad range of complex electronic quantum systems showing frustrated phase separation (Kugel *et al.*, 2008) and displaying phenomena such as peculiar magnetism, two-dimensional electron gases, unconventional superconductivity (Poccia *et al.*, 2017), photovoltaic energy conversion, spintronics and heterogeneous catalysis will become possible with X-ray beams in novel DLSRs.

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