Excitons : A Comprehensive Summarization

In this project, we aim to provide a complete and concise overview of excitons: their history, origin, behavioral characteristics and their importance in the physical world and research. Excitons are quasiparticles that have helped shape our fundamental understanding of nanomaterials, so it is important to have a thorough knowledge about them before we can conduct research on particles belonging to the nanoscale.

1 Introduction

Russian physicist Yakov Frenkel described the stimulation of atoms in an insulator lattice in 1931, which is when the idea of excitons was originally put out. He suggested that this excited state may move across the lattice like a particle without a net transfer of charge.

An exciton is a bound state consisting of an electron and an electron hole attracted to each other by the electrostatic Coulomb attraction. It is a non-electrically charged quasiparticle found in insulators, semiconductors, and certain liquids. A quasiparticle is defined as a composite entity (such as a vibration in a solid) that is analogous in its behavior to a single particle. The exciton is defined as an elementary excitation of condensed matter capable of conveying energy, but not net electric charge.
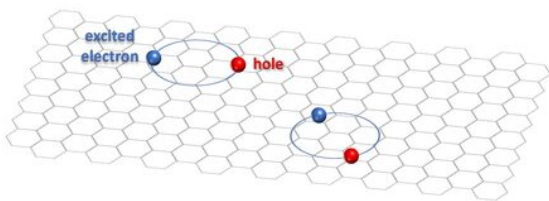

FIGURE 1. Visualization of an exciton

An exciton forms when a material absorbs a photon of higher energy than its bandgap. This causes an electron to be excited from the valence band into the conduction band. As a result, a positively charged electron hole is left behind, which is an abstraction for the place from where an electron was displaced. Because of the repulsive Coulomb forces from the huge number of electrons around the hole and excited electron, the electron in the conduction band is less attracted to this localised hole. These repelling forces maintain a stable energy balance. As a result, the exciton has somewhat less energy than an unbound electron and hole. The bound state's wavefunction is said to be hydrogenic, which is an exotic atom state similar to that of a hydrogen atom.

Researchers are interested in excitonic phenomena ranging from optical, quantum-optical, and thermodynamic transitions to the hypothetical condensation of excitons into a quantum-degenerate state due to the numerous similarities between excitons and the hydrogen atom. Excitonic fingerprints are frequently observed in direct-gap semiconductor optical absorption and emission.

The binding energy, however, is substantially lower, and the particle is much bigger than a hydrogen atom. This is due to both the Coulomb force being screened by other electrons in the semiconductor (i.e., its relative permittivity) and the excited electron and hole having small effective masses. The decay of the exciton is restricted by resonance stabilisation owing to the overlap of the electron and hole wave functions, resulting in a longer lifespan for the exciton. The spins of the electron and hole might be parallel or anti-parallel. The exchange interaction couples the spins, resulting in exciton fine structure. The characteristics of an exciton in periodic lattices are momentum dependent.

Recent advances in research has shown xcitons to play major roles in determining the behavior of a system. Monolayers of a transition metal dichalcogenide (TMD) are an excellent and cutting-edge example in which excitons play a significant role. They have a bounding energy on the order of 0.5 eV in these systems, with a higher Coulomb attraction between the hole and the electrons than in other classical quantum wells. As a result, optical excitonic peaks are present even at room temperature in these materials.

Excitons are frequently studied in the two limiting scenarios of small dielectric constant vs big dielectric constant, which correspond to Frenkel and Wannier-Mott excitons, respectively.

2 Types of Excitons

2.0.1 *Frenkel exciton*

In materials with a low dielectric constant, the Coulomb contact between an electron and a hole can be strong, and excitons tend to be tiny, of the same order as the unit cell size. These excitons are termed as "Frenkel Exciton". Molecular excitons can even reside on the same molecule, as

in fullerenes. The binding energy of this Frenkel exciton, named after Yakov Frenkel, is typically in the range of 0.1 to 1 eV. Frenkel excitons are commonly observed in alkali halide crystals and organic molecular crystals made up of aromatic compounds like anthracene and tetracene. On-site d-d excitations in transition metal compounds with partially-filled d-shells are another example of Frenkel exciton. While symmetry prohibits d-d transitions in theory, they become weakly permitted in a crystal when the symmetry is violated by structural relaxations or other factors. Absorption of a photon resonant with a d-d transition produces an electron-hole pair on a single atomic site, which is known as a Frenkel exciton.
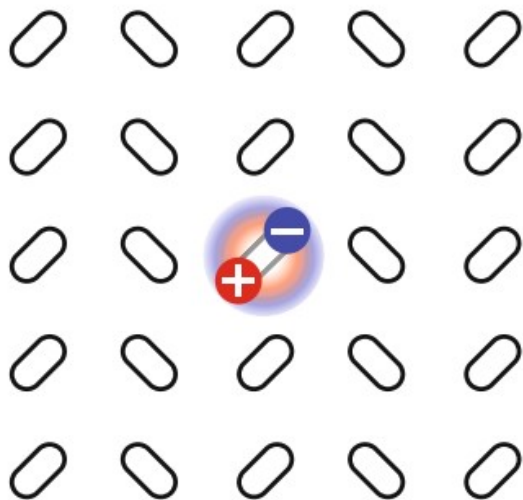

FIGURE 2. Exciton with a small radius localized at a molecule in an organic crystal or an atom in an organic crystal (Frenkel exciton)

The local electronic excitations of the molecules interact with each other via the Coulomb potential, which leads to a splitting of the electronic transitions. This process is known as Davydov splitting in molecular crystals, and it may be observed when two interacting molecules create a unit cell. In general, the interplay of local excitations in molecular assemblies such as aggregates causes a distinct shift in the absorption bands. J- and H-aggregates are distinguished here by their red and blue shifts in relation to monomer absorption. While excitons in molecular crystals (for example, polyacenes) have been researched for decades, Frenkel excitons in molecular nanoscale systems have lately received a lot of interest. These include conjugated polymers, molecular aggregates, and photosynthetic pigment protein complexes. What distinguishes nanoscale systems from crystals is their flexibility, which facilitates the tuning of the optical and transport properties.

The recent research interest in nanomaterials have resulted in breakthroughs in knowing the true nature and behavior of Frenkel Excitons. For example, the role of Frenkel Excitons has been observed in biological systems as well. Light harvesting and charge separation are realized in pigment-protein complexes, where reaction centers responsible for charge separation are surrounded by antennae capturing photons and transferring the excitation energy by means of Frenkel excitons.

2.0.2 Wannier–Mott exciton

In semiconductors, the dielectric constant is generally large. As an outcome, electric field screening decreases the Coulomb interaction between electrons and holes. The result is a Wannier–Mott exciton, which has a radius larger than the lattice spacing. The small effective mass of electrons found in semiconductors supports large exciton radii. As a result, the influence of the lattice potential may be integrated into the electron and hole effective masses. Similarly, due to the smaller masses and the screened Coulomb interaction, the binding energy is often significantly lower than that of a hydrogen atom, on the order of 0.01eV. This type of exciton was named for Gregory Wannier and Nevill Francis Mott. Wannier-Mott excitons are most commonly observed in semiconductor crystals with narrow energy gaps and high dielectric constants, but they have also been detected in liquids such as liquid xenon. They are also known as large excitons. Wannier-Mott excitons can be expressed with the help of a model similar to that of the Hydrogen atom.
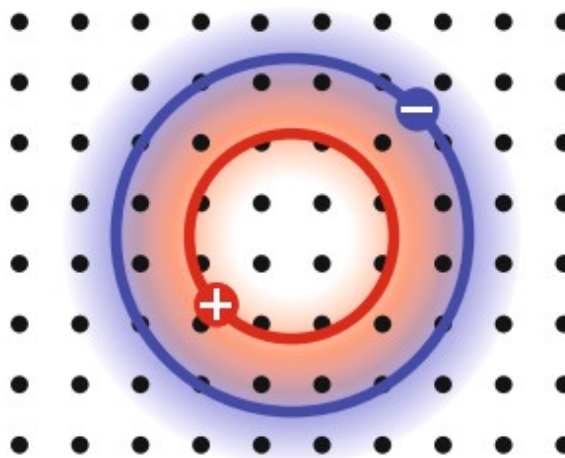

FIGURE 3. Exciton with a large radius extending over many lattice constants and a center of mass slightly shifted toward the heavier hole (Wannier–Mott exciton).

The ionization energy of Wannier-Mott excitons in typical semiconductors is on the order of 10 meV; hence, the thermal energy kT at room temperature (26 meV) is sufficient to dissociate most of them.

Equations for 3D semiconductors:

In a bulk semiconductor, a Wannier exciton has an energy and radius associated with it, called exciton Rydberg energy and

exciton Bohr radius respectively. For the energy, we have :

$$E(n) = -\frac{\left(\frac{\mu}{m_0\varepsilon_r^2}\mathrm{Ry}\right)}{n^2} \equiv -\frac{R_X}{n^2}$$

where Ry is the Rydberg unit of energy, ε_r is the is the (static) relative permittivity, μ is the reduced mass of the electron and hole, and m_0 is the electron mass. Concerning the radius, we have :

$$r_n = \left(\frac{m_0\varepsilon_r a_H}{\mu}\right)n^2 \equiv a_X n^2$$

where a_H is the Bohr Radius.

Equations for 2D semiconductors:

The system is quantum confined in the direction perpendicular to the plane of the material in two-dimensional (2D) materials. The system's lower dimensionality affects the binding energies and radii of Wannier excitons. Moreover, excitonic effects are amplified in such systems.

For a simple screened Coulomb potential, the binding energies take the form of the 2D hydrogen atom :

$$E(n) = -\frac{R_X}{\left(n - \frac{1}{2}\right)^2}$$

In most 2D semiconductors, the Rytova-Keldysh form is a more accurate approximation to the exciton interaction :

$$V(r) = -\frac{\pi}{2r_0}\left[\mathrm{H}_0\left(\frac{\kappa r}{r_0}\right) - Y_0\left(\frac{\kappa r}{r_0}\right)\right]$$

where r_0 is the so-called screening length, κ the average dielectric constant of the surrounding media, and r the exciton radius. For this potential, no general expression for the exciton energies may be found. One must instead turn to numerical procedures, and it is precisely this potential that gives rise to the non-hydrogenic Rydberg series of the energies in 2D semiconductors.

2.0.3 Charge-transfer exciton

The charge-transfer exciton is an intermediate instance between Frenkel and Wannier excitons. Charge Transfer excitons develop in molecular physics when an electron and a hole occupy neighbouring molecules. Charge Transfer excitons, unlike Frenkel and Wannier excitons, have a static electric dipole moment and are found largely in organic and molecular crystals.

Charge Transfer excitons may also be found in transition metal oxides, when an electron in the transition metal 3d orbitals and a hole in the oxygen 2p orbitals are involved. Examples are the lowest-energy excitons in linked cuprates and the TiO2 two-dimensional exciton. Regardless of its origin, the idea of Charge Transfer exciton is always associated with a charge transfer from one atomic site to another, thereby

spreading the wave-function over a few lattice sites.

Understanding Charge Transfer excitons is essential to the development of excitonic solar cells. In a conventional p-n junction solar cell, the built-in potential separates the photoexcited electron and hole. In contrast, there may not be a built-in potential in an excitonic solar cell, and charge separation requires an energetic driving force provided by the differences in the electronic levels of the materials at the interface, i.e., a donor/acceptor interface. When the electron donor and/or acceptor are organic semiconductors, the low dielectric constants ensure that charge separation at the D/A interface does not give free charge carriers but rather a bound electron-hole pair across the interface, i.e., a Charge Transfer exciton.

As Charge Transfer electrons are important quasiparticles for optoelectronic applications of semiconducting heterostructures several methods have been developed to help examine and learn about them. Effective control of charge-transfer excitons by the electric field has been achieved, and various optoelectronic devices have been based on them. Because of the separation of electrons and holes in both the real and momentum space, charge-transfer excitons have shown long lifetimes and novel spin/valley properties.

Using time-resolved two-photon photoemission (TR-2PPE) spectroscopy, we can examine Charge Transfer excitons on crystalline organic semiconductor surfaces. In a TR-2PPE experiment, two femtosecond laser pulses are focused onto the sample surface (with photon energy generally below the work function), and the resultant photoelectron due to two-photon excitation is measured in an electron energy analyzer. Time-resolved two-photon photoelectron spectroscopy often makes use of both ultrafast optical technology and ultrahigh vacuum components. UV light is often necessary to photoemit electrons. To facilitate investigations on the population and relaxation pathways of the excitation, this measurement is performed at different time delays.

This technique has been used for many different types of materials to study a variety of exotic electron behaviors, including image potential states at metal surfaces, and exciton dynamics at molecular interfaces, especially Charge Transfer Excitons.
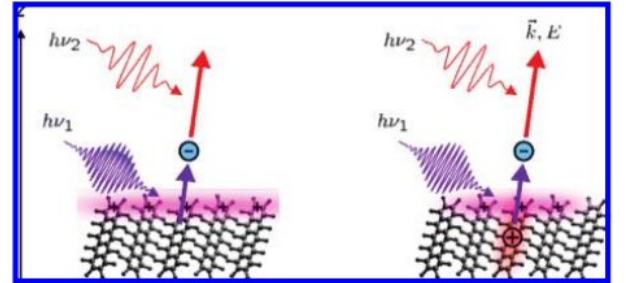

FIGURE 4. . Probing image potential states (left) and CT excitons (right) on an organic semiconductor surface by TR-2PPE.
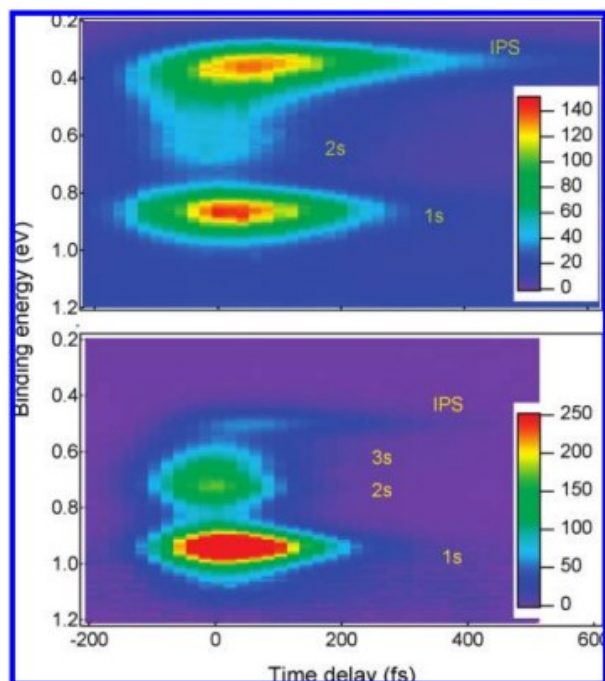
FIGURE 5. Pseudo-color plots of TR-2PPE spectra at different pump-probe delay times for 1 ML pentacene/Bi. Each vertical cut corresponds to an electron energy-resolved 2PPE spectrum at a particular pump-probe delay. The color scale is photoelectron intensity (10^3 counts/s). The binding energy scale is referenced to the vacuum level.
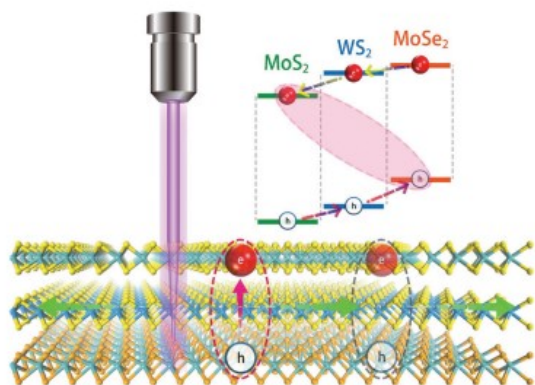

FIGURE 6. Schematics of the charge-transfer exciton dynamics studied. A laser pulse excites electron–hole pairs in all three layers of the trilayer sample. Charge-transfer excitons are formed and then diffuse laterally in the sample.

2.0.4 Atomic and Molecular Excitons

An exciton may also be defined as an excited state of an atom, ion, or molecule that is travelling from one cell of the lattice to another.

When a molecule absorbs a quantum of energy that corresponds to a transition from one chemical orbital to another, the resulting electronic excited state is also known as an exciton. An electron is said to be located in the lowest vacant

molecular orbital and an electron hole in the highest occupied molecular orbital, and the electron-hole state is said to be bound since they are found within the same molecular orbital manifold.

Molecular excitons generally have characteristic lifetimes on the order of nanoseconds, after which the molecule returns to its ground electronic state and emits photons or phonons. Molecular excitons have various intriguing qualities, one of which is energy transfer, which occurs when a molecular exciton has adequate energetic matching to the spectrum absorbance of a second molecule. Because the process is very sensitive on the intermolecular distance between the species in solution, it has found applications in sensing and molecular rulers.

The defining characteristic of molecular excitons in organic molecular crystals are doublets and/or triplets of exciton absorption bands strongly polarised along crystallographic axes. An elementary cell in these crystals consists of many molecules sitting in symmetrically similar places, resulting in level degeneracy lifted by intermolecular contact. As a result, absorption bands are polarised along the crystal's symmetry axes. Antonina Prikhot'ko[19][20] identified such multiplets, and Alexander Davydov postulated their origin. It is referred to as 'Davydov splitting.'

2.0.5 Surface exciton Polaritons

A surface exciton polariton (SEP) is an elementary excitation resulting from the coupling of photons to excitons at the surface of a crystal. SEPs propagate along the boundary between an outside dielectric medium and a crystal which has Wannier-type excitons as elementary bulk excitation.

SEPs have been observed experimentally in various inorganic semiconductors, including ZnO, CuBr, CuCl, and ZnSe. However, successful observation of SEPs in these media requires cryogenic temperature, which limits their practical applications. This limitation is because the excitons in these inorganic semiconductors are Wannier-Mott excitons, which have low binding energy (approximately 10 meV) below the thermal energy at room temperature (25 meV). In contrast, excitons in organic crystals are Frenkel excitons, with much higher binding energy (approximately 1 eV), which allows the observation of SEPs in organic crystals at room temperature. SEPs in organic materials were experimentally demonstrated at room temperature in the 1970s.

The SEPs were observed in the Otto configuration, where the metal film was replaced with anorganic crystalline solid. In these experiments, a specific crystal face was required for the observation of SEPs. In 2017, by replacement of the metal thin film in the traditional Kretschmann-Raether configuration with an organic noncrystalline medium, SEPs were experimentally observed under 532-nm illumination at room temperature.
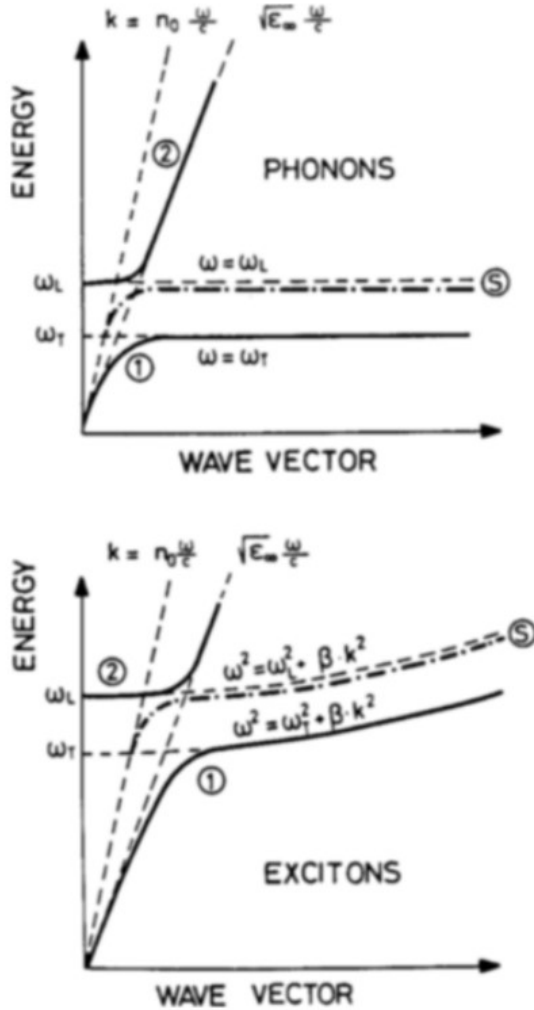
FIGURE 7. Schematic energy versus real wave-vector dispersion relations for phonon polaritons without spatial dispersion (upper part) and exciton polaritons with spatial dispersion (lower part). The symbols (I) and (2) denote the lower and upper bulk polariton branches, (S) the surfaee-polariton dispersion curves.

The coexistence of more than one polariton branch at a givenenergy is an immediate consequence of the wavevector dependence of the exciton energy, the spatial dispersion. The lower part of Fig. 7 shows two transverse and one longitudinal bulk mode at a givenfrequency above coL- Also below the longitudinal resonance frequency, one always has to deal with threemodes, the wave vectors of two of them, however, are purely imaginary and therefore are not shown in Fig. 7.

2.0.6 *Spatially direct and indirect excitons*

Usually, excitons in a semiconductor have a very short lifetime due to the close proximity of the electron and hole. However, 'spatially indirect' excitons may be generated by placing the electron and hole in spatially separated quantum wells with an insulating barrier layer in between. Unlike typical (spatially direct) excitons, these spatially indirect exci-

tons can have a wide spatial separation between the electron and hole, giving them a substantially longer lifetime. This is frequently used to chill excitons to extremely low temperatures in order to investigate Bose-Einstein condensation (or rather its two-dimensional analog). It is found that the ground state of the indirect excitons formed by electrons and holes and spatially separated between neighboring quantum wells lies between the ls ground state of the direct excitons and the continuum threshold for dissociated exciton states in the minibands. Indirect excitons in superlattices have a significant oscillator strength when the binding energy of the exciton exceeds the order of the width of the resulting miniband.

3   Self Trapping of Excitons

Excitons interact with phonons, or lattice vibrations, in crystals. Excitons are dispersed by phonons when the coupling is weak, as in typical semiconductors such as GaAs or Si. When the connection is strong enough, excitons can self-trap. Self-trapping causes excitons to be dressed with a thick cloud of virtual phonons, which severely limits excitons' ability to migrate across the crystal. In layman's words, this means that the crystal lattice deforms locally around the exciton. Self-trapping can occur only if the energy of the deformation is large enough to compete with the breadth of the exciton band. As a result, it should be on an atomic scale, around one electron volt.

Self-trapping of excitons is comparable to the formation of strong-coupling polarons, but there are three key distinctions. Due to their electric neutrality, self-trapped exciton states always have a tiny radius, on the order of the lattice constant. Second, a self-trapping barrier separates free and self-trapped states, implying that free excitons are metastable. Third, this barrier allows free and self-trapped excitons to coexist. This implies that spectral lines of free excitons and broad bands of self-trapped excitons can be detected in absorption and luminescence spectra at the same time.

While the self-trapped states are of lattice-spacing scale, the barrier has typically much larger scale. Its spatial scale is about $r_b \sim m\gamma^2/\omega^2$ where m is effective mass of the exciton, γ is the exciton-phonon coupling constant, and ω is the characteristic frequency of optical phonons. Excitons are self trapped when m and γ are large, and then the spatial size of the barrier is large compared with the lattice spacing. Transforming a free exciton state into a self-trapped one proceeds as collective tunneling of coupled exciton-lattice system (an instanton). Because r_b is large, tunneling can be described by a continuum theory. [29] The height of the barrier is $W \sim \omega^4/m^3\gamma^4$.

Because both m and γ appear in the denominator of W, the barriers are basically low. Therefore, free excitons can be seen in crystals with strong exciton-phonon coupling only in pure samples and at low temperatures. Coexistence of free and self-trapped excitons was observed in rare-gas solids, alkali-halides, and in molecular crystal of pyrene.

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