

Physics 211A Special Topic Paper

Scientist: Yakov Frenkel

Paper: On the Transformation of Light into Heat in Solids I

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Introduction

Jakov Frenkel was a Russian born physicist who made multiple contributions to fields both within and outside of condensed matter physics. His book *Kinetic Theory of Liquids*, is a classic text on the subject [1]. He has also made contributions to semiconductor physics, specifically in coming up with the Poole-Frenkel effect [2]. One of his most important contributions was the introduction of Frenkel Excitons, in his paper *On the Transformation of Light into Heat in Solids I*, although he certainly did not refer to the excitations he studied as "Frenkel Excitons," in the paper [3]. This is the topic that I will present in this report. Frenkel's paper has garnered over 540 citations. Although this is impressive, it doesn't even begin to capture the influence of Frenkel's work. Excitons are bound states made up of an electron and a hole, and have become their own sub-field of condensed matter physics, with some labs devoted completely to their study. The excitons studied in Frenkel's work, Frenkel Excitons, are only one type of exciton. As will be discussed further below, Frenkel Excitons are highly localized excitons, where the hole and electron are less than a lattice constant from each other and are localized to the same atom in the crystal. This is in contrast to other kinds of excitons, such as Wannier Excitons, where the distance between the electron and hole can be larger than a lattice constant, and the electron and hole are not necessarily localized to the same atom on the crystal [4].

Initial Exciton Calculation

In [3], Frenkel tries to address the issue of how a model of a solid consisting of essentially harmonic oscillators can take in the energy of absorbed light. It is well known that when light is absorbed by a single molecule, an electron in the molecule will jump to a higher energy, excited state. Although it is fairly intuitive how single photons can also cause electrons to jump to excited states in crystals, it is not obvious what the effects of excited electronic states are on the entire crystal. Frenkel's first conceptual leap was that, instead of the excited electronic state being localized to a single atom/molecule (unit cell), the excitation can actually be spread over the crystal, in "Excitation Waves." Frenkel first introduces these, and studies their properties in detail; this is essentially where the notion of excitons is introduced [3].

There are some clear assumptions in [3]. The coupling between atoms in the crystal is assumed to be small, specifically compared to the coupling between the electrons and the atoms. It is also assumed that each electron stays fixed to its own atom. The vibratory motion of the atoms is also neglected at first, until later in the paper when the relationship between the excitons and the heat oscillators (normal modes) is developed [3].

Due to absorption of light, the electronic state of an atom can change from the ground state to an excited state, where one of the valence electrons moves to a higher energy state, leaving a hole in its previous state. The different states of the crystal, in the presence of a single excitation, are then linear combinations of the states where the excitation is on each of the different atoms. For n atoms, there are n sets of coefficients c_n characterizing the different states:

$$\Psi = \sum_{l=1}^n c_l \phi_l \quad (1)$$

$$\phi_1 = \psi_{II}(1)\psi_I(2)\dots\psi_I(n), \quad \phi_2 = \psi_I(1)\psi_{II}(2)\dots\psi_I(n), \quad \dots \quad (2)$$

Here ψ_I refers to the ground state electron configuration of an atom, and ψ_{II} refers to the excited state electron configuration. Then ϕ_n refers to the state where the n th atom is in the excited electronic state and all of the other atoms are in the ground state (the argument of ψ refers to the coordinate of the electron in that atom). The set of possible states is referred to as

the excitation multiplet. The coefficients are found by solving the matrix equation

$$\sum_{l=1}^n U_{kl} c_l = W' c_k \quad (3)$$

Where U_{lk} are the matrix elements of the potential energy of the atoms and W' is the difference between the energies of the different states (really the set of coefficients c_l and W' have an index for each of the n solutions to the equations (3)). U_{lk} is calculated using the potential energy between two electrons separated by a distance $R_{\alpha\beta}$.

$$U = \sum_{\alpha < \beta} U(\alpha, \beta; R_{\alpha\beta}) \quad (4)$$

$$U_{kl} = \int \dots \int U \phi_k^* \phi_l d\tau_1 \dots d\tau_n \quad (5)$$

What can be noticed about the equations in (3) is how much they resemble the equations for classical, coupled harmonic oscillators, with c_l representing the amplitudes of the different oscillations, $\sqrt{W'}$ representing the classical frequencies, and U_{lk} representing the coupling coefficients between the oscillators. It should be made clear again that in reality, the c_l are the amplitudes for which atom contains the excited electronic state.

At this point, [3] now assumes a rectangular or parallelepiped lattice in order to make a concrete calculation. In this case, the normal modes of vibration are standing waves with the following wave numbers:

$$g_1 = \pm \frac{r_1}{2a_1}, \quad g_2 = \pm \frac{r_2}{2a_2}, \quad g_3 = \pm \frac{r_3}{2a_3} \quad (6)$$

With r_i the index associated with the different wavenumbers in the i th direction (x, y, or z), ranging from 0 to $n_i - 1$, n_i being the total number of atoms in the i th direction. Similarly, the a_i are the edges of the crystal. The solutions to the equations in (3) can be written in the following form [3]:

$$c_{r_1, r_2, r_3, k_1, k_2, k_3} = A_{r_1 r_2 r_3} \cos \frac{\pi \delta k_1 r_1}{a_1} \cos \frac{\pi \delta k_2 r_2}{a_2} \cos \frac{\pi \delta k_3 r_3}{a_3} \quad (7)$$

Where $A_{r_1 r_2 r_3}$ is an overall normalization constant, and r_i indexes the different solutions, with one separate index for each spatial dimension. Plugging this solution into (3) can help us find W' :

$$W'_{r_1 r_2 r_3} = \sum_{l_1 l_2 l_3} U_{000 l_1 l_2 l_3} \cos \frac{\pi \delta l_1 r_1}{a_1} \cos \frac{\pi \delta l_2 r_2}{a_2} \cos \frac{\pi \delta l_3 r_3}{a_3} \quad (8)$$

Here the first index in U_{kl} was set to 0 by translation invariance. Up to now we have been general about U_{kl} , we can then look at the case of nearest neighbor coupling, here the previous expression becomes

$$W'_{r_1 r_2 r_3} = V_0 + 2V_1 \left(\cos \frac{\pi \delta}{a_1} + \cos \frac{\pi \delta}{a_2} + \cos \frac{\pi \delta}{a_3} \right) \quad (9)$$

Where V_1 is the potential energy matrix element, calculated with equation (5), for nearest neighbors, and V_0 is six times the potential energy matrix element calculated for the same atom. From this, we can then identify this energy with the frequency associated with this excited state of the crystal. The reason that this is useful is that we can then calculate the group velocity for this excited state [3].

$$h\nu' = W', \quad v_i = \frac{\partial \nu'}{\partial g_i} = \frac{-4\pi \delta V_1}{h} \sin 2\pi g_i \delta \quad (10)$$

Which in the small g_i limit reduces to

$$\vec{v} = \frac{-8\pi^2 \delta^2 V_1}{h} \vec{g} \quad (11)$$

An important thing to note about this result is that the group velocity is proportional to the interaction matrix element/energy. This captures the fact that the probability for an excited electronic state to be transmitted from one atom to another is larger for nearby atoms, as the interaction matrix element is largest for nearest neighbors. Taking the small g_i limit shows that, in this limit, the propagation is parallel to the wavevector of the state, similar to other particle-like states in quantum mechanics. With the coefficients c_l , one can create standing waves or wavepackets with suitable combinations of states with different values of g_i .

The argument just given seems somewhat simple and straightforward, but the implications are very important. The fact that the excitation, meaning the atom with the excited state, can move and show particle-like properties really tells us that it behaves like a particle, which has been dubbed the exciton. Specifically, when the electron is excited to a higher energy state within the atom, it leaves behind a vacancy in the state that it previously occupied, a hole. This electron-hole pair forms the exciton, and Frenkel's calculations show that they, together, show properties of a single particle [3]. Excitons have become their own subfield of condensed matter physics, and

Frenkel excitons are only one limiting case, where the electron and hole are localized to the same atom. Wannier calculated some of the properties of the excited states of electronic crystals more from the perspective of energy bands, and also found that the spectrum of states contains a section, below the Bloch Band, consisting of the excitonic states of a bound electron-hole pair [4]. Wannier found the lowest lying excitons resembled Frenkel Excitons, where the electron and hole were localized on the same atom. However, there were also excitons closer in energy to the bands, and the orbit of the electron there is determined more by the coulomb interaction with the hole the electron is bound to. Since an electron-hole pair is electrically neutral, no photocurrent is observed in this region. Above this spectrum of states current can be observed as there the electrons and holes move independently from each other. The relationship between Frenkel Excitons and Wannier Excitons is similar to the relationship between tight binding calculations and band theory calculations, one involves electrons more localized to the ions in the crystal, the other involves electrons more spread out in the crystal compared to the ions.

Further Exciton Calculations due to Frenkel

After the initial calculation of excitons and some of their properties, Frenkel's paper next calculates the effect that excitons can have on the properties of a crystal [3]. First, we can look at the speed of sound, which is given by

$$u = \sqrt{\frac{\kappa}{\rho}} \quad (12)$$

Where κ is the elastic modulus of the crystal and ρ is the mass density. Both of these change in the excited states of the crystal. In the non-excited state, the elastic modulus can be calculated by expanding the mutual potential energy between the atoms in the crystal, W_0 :

$$W_0 = W_0^0 + \frac{1}{2} \left(\frac{\partial^2 W_0}{\partial v^2} \right)^0 (v - v^0)^2, \quad \kappa_0 = v_0^0 \left(\frac{\partial^2 W_0}{\partial v^2} \right) \quad (13)$$

With v referring to the volume of the crystal (so that the above describes stretching and compressing of the crystal). Also, for a cubic crystal, the mass density is given by $\rho_0 = \frac{m}{\delta_0^3}$. The same calculation can then be done with

the excited state mutual potential energy. Taylor expanding the energy in the change in the lattice constant, $\Delta\delta_r = \delta_r - \delta_0$ (due to the excited state), and using the fact that we are expanding around a minimum of the potential energy gives

$$\frac{\partial W_r}{\partial \delta_r} = \frac{\partial W_0}{\partial \delta} + \frac{\partial^2 W_0}{\partial \delta^2} \Delta\delta_r + \frac{\partial W'_r}{\partial \delta} = 0 \quad (14)$$

$$\Delta\delta_r = -\frac{\partial W'_r}{\partial \delta} / \frac{\partial^2 W_0}{\partial \delta^2} \quad (15)$$

Then using our expression for the energy of the excited state, equation (9), the change in the lattice constant is found to scale as $\frac{1}{n}$ since V_1 doesn't scale with n . This result can be used with the expressions for the elastic modulus and mass density, to see that the change in these quantities due to an excited state also scales as $\frac{1}{n}$. Here n is the number of atoms in the crystal, and is a huge number, so the direct changes to these quantities will be too small to detect.

The significant effect that the excited electron states can have on the crystal is that radiationless transitions from the excited electronic state to an unexcited state are possible, with the difference in energy being converted into vibrational motion [3]. Specifically, Frenkel refers to the vibrational normal modes of the crystal as "heat oscillators," which have harmonic oscillator wavefunctions in the normal coordinates ξ_n .

$$f_N(\xi) = [2^N N! (\pi\alpha)^{1/2}]^{-1/2} H_N(\alpha^{1/2}\xi) e^{-1/2\alpha\xi^2} \quad (16)$$

$$\alpha = 4\pi^2\nu m/h \quad (17)$$

The relationship between the normal modes in the unexcited state $\xi_1 \dots$ and in the excited state $\xi_{r_1} \dots$ can be developed, the details of which can be found in [3], which is necessary to calculate the probability of radiationless transitions between the excited and unexcited states. This is approached with perturbation theory, by looking at the matrix element of the perturbation energy with respect to the wavefunctions of the electronic and vibrational degrees of freedom.

$$M_r = \int U \Psi_0^* \Psi_r = \int \dots \int U \chi_0^* \chi_r d\tau_1 \dots d\tau_n \prod_{s=1}^{3n} f_{N_{0s}}(\xi_s) f_{N_{rs}} \left[\left(\frac{\nu_{rs}}{\nu_{0s}} \right)^{1/2} \xi_s \right] d\xi_s \quad (18)$$

Where χ refers to the electronic wavefunction, $f(\xi)$ to the wavefunction of the normal modes, ν_{0s} to the unexcited frequencies, and ν_{rs} to the excited state frequencies. The dominant processes will be at or near resonance, which means that the energy conservation condition will be satisfied or nearly satisfied.

$$W_{II} - W_I + W'_r - W'_0 + \sum_{s=1}^{3n} \left[h\nu_{rs} \left(N_{rs} + \frac{1}{2} \right) - h\nu_{0s} \left(N_{0s} + \frac{1}{2} \right) \right] = 0 \quad (19)$$

Here W_I is the ground state energy of a given electronic state and W_{II} is the excited state energy. This also lends itself to looking at radiative transitions, which are related to absorption and emission of light. In this case, the resonance condition, instead of having the change in energy equal to 0, it is instead planck's constant times the frequency of absorbed/emitted light [3].

$$h\nu = W_{II} - W_I + W'_r - W'_0 + \sum_{s=1}^{3n} \left[h\nu_{rs} \left(N_{rs} + \frac{1}{2} \right) - h\nu_{0s} \left(N_{0s} + \frac{1}{2} \right) \right] \quad (20)$$

Further Developments in Exciton Physics

There has been a substantial amount of experimental and theoretical work on excitons since Frenkel's work, too much to give a complete summary in this short paper, so instead I will highlight some particularly interesting developments. For example, charge-transfer excitons are an intermediate case between Frenkel and Wannier excitons, where the electron and hole are not on the same molecule or largely separated, but stay on neighboring molecules, and have been seen in organic molecules and ionic compounds [5]. Excitons are bosons, and theoretically were predicted to be able to form Bose-Einstein Condensates [6]. One of the first people to observe Bose-Einstein Condensation of Excitons is a professor at UCSD, Dr. Leonid Butov [7]. In these experiments, indirect excitons were used. Indirect excitons are fairly different from Frenkel Excitons, in that the electron and hole are highly nonlocalized from each other. Specifically, for indirect excitons the electron and hole are in different, spatially separated layers of quantum wells.

Exciton research is still very active today. There was interesting recent paper [8] which involved an experiment on electron emission in diamond needles that appealed to excitons as an explanation for experimental results. The experiment essentially sent laser pulses of light (of varying frequency/energy)

onto the backside of diamond needles. Electron emission from the tip of the diamond needle was then measured, specifically the dependence of the emitted current on an applied voltage and on the energy of the illuminating light. An interesting puzzle arises in this experiment, namely that the penetration depth for light in diamond is $\approx 5\mu m$, while the distance between the point of illumination and the point of emission is $\approx 100\mu m$, so the region of carrier generation is not the same as that of emission. An explanation proposed by the authors of the paper is that the absorbed light could be creating excitons, which can travel as wave packets to the tip of the needle. There, or along the way, the applied field can turn the exciton into a free carrier, where the electron can then be emitted. Some supporting evidence for this explanation is that, at a constant bias voltage, the threshold for a significant increase in the emitted current is around 5.2eV, which is the energy of the excitons in diamond [8].

Conclusion

As stated earlier, the impact of Frenkel's work is not fully captured by how many citations it has. The purpose of this work was essentially to look at how excited electronic states can affect the properties of a crystal, but it was found that these excited electronic states can move and act like particles themselves. This conceptual leap gave us excitons, which along with pioneering work from Wannier and many others afterward, became a significant subfield of condensed matter physics, which is now covered in most solid state textbooks [9, 10]. Exciton physics is still a very active field today. A professor at UCSD, Leonid Butov, is one of the current leaders of exciton physics, and has even started to make devices that use properties of excitons [11]. Frenkel's paper is also still being cited this year, with 24 citations in 2018, the most recent being October 29th [12]. It is quite impressive and a bit unexpected (to me) that a question as simple as "What are the effects of individual excited electronic states on a crystal," can have such large implications and spawn a field of physics.

References

- [1] J Frenkel. *Kinetic Theory of Liquids*. Dover Publications, Mineola, New York, 1955.
- [2] J Frenkel. *On pre-breakdown phenomena in insulators and electronic semi-conductors*. Physical Review, 54:647, 1938.
- [3] J Frenkel. *On the Transformation of Light into Heat in Solids I*. Physical Review, 37:17-44, 1931
- [4] G Wannier. *The Structure of Electronic Excitation Levels in Insulating Crystals*. Physical Review, 52:191-197, 1937
- [5] V Agranovich. *Excitations in Organic Solids*. Oxford University Press, Oxford, New York, 2008
- [6] V Agranovich and B Toshich *Collective Properties of Frenkel Excitons*. Soviet Physics JETP, 26(1):104-112, 1968
- [7] L. Butov, C Lai, A Ivanov, A Gossard, and D Chemla *Towards Bose-Einstein condensation of excitons in potential traps*. Nature, 417:47-52, 2002
- [8] V Porshyn, V Kleshch, E Obraztsova, A Chuvilin, D Lutzenkirchhecht, and A Obraztsov *Photoinduced effects in field electron emission from diamond needles*. Applied Physics Letters, 110, 2017
- [9] N Ashcroft and N Mermin *Solid State Physics*. Harcourt College Publishers, Orlando, Florida, 1976
- [10] E Kaxiras *Atomic and Electronic Structure of Solids*. Cambridge University Press, Cambridge, United Kingdom, 2003
- [11] A High, A Hammack, L Butov, and A Gossard *Exciton optoelectronic transistor*. Optics Letters, 32:2466-2468, 2007
- [12] K Kamide, T Mochizuki, H Akiyama, and H Takato *Nonequilibrium Theory of the Conversion Efficiency Limit of Solar Cells Including Thermalization and Extraction of Carriers*. Physical Review Applied, 10(4),2018