

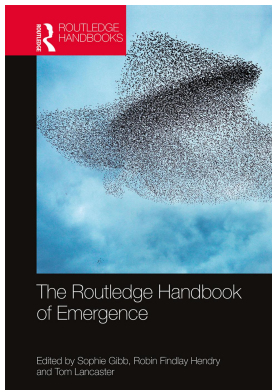
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### **Emergence in Non-Relativistic Quantum Mechanics**

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## EMERGENCE IN NON-RELATIVISTIC QUANTUM MECHANICS

*Stewart Clark and Iorwerth Thomas*

### Introduction

Materials are a collection of atoms, which consist of atomic nuclei surrounded by electrons, and these interact with each other electrostatically by means of quantum mechanics via Coulomb's law. These are the “parts” that make up materials. One conception of emergence is that new properties arise out of combinations of these parts, so that a material (solid, liquid, molecule, etc.) has properties that the parts do not. In this chapter we will discuss examples of how properties emerge from the parts when described using only non-relativistic quantum mechanics. This is often called a *first-principles* approach. One of the most challenging problems in condensed matter physics today is predicting the properties of materials from first principles, that is, from knowledge of the nuclei, electrons and their interactions, but without the requirement of additional experimental information. Can we take a simple description of a material and give insight into its emergent properties? Can we predict the properties of everyday materials and objects around us, both simple and complex, ranging from metals to glasses, to complex technological materials and biological systems?

Materials can be described, in principle, by the Schrödinger equation (Schrödinger 1926). Quantum mechanics provides a reliable way to calculate what electrons and atomic nuclei do in any situation. The behaviour of electrons, in particular, governs most of the properties of materials. This is true for a single atom, or for assemblies of atoms in condensed matter, because quantum mechanics describes, explains and allows us to define a rich variety of properties, for example, chemical bonds. Therefore, being able to solve the Schrödinger equation would give us a great deal of information about material systems. However, there are two issues here: (i) it is a tremendously difficult task mathematically and computationally to solve the Schrödinger equation for anything but the simplest cases; and (ii) if we could, the amount of data and information that is gained is huge, and so it would be a technological challenge to find emergent properties of materials from these data. Exact, closed-form (pencil-and-paper, mathematical) solutions of the Schrödinger equation exist only for a single electron in exceptionally simple situations. The problem of interacting electrons in condensed matter physics, a manifestation of the *many-body problem*, is the defining challenge of the subject.

This chapter is concerned with how we can deal with these issues. The discussion will allow us to comment on emergent properties that arise from consideration of non-relativistic quantum

mechanics. Specifically, we will describe some examples of emergent properties that can be found by investigating solutions of the Schrödinger equation for realistic, complex systems.

The difficulty in solving the Schrödinger equation for materials, and analysing the data to identify emergent properties, could be called the *fundamental problem of condensed matter physics* – as regardless of whether you are a friend of emergence or the most stringent reductionist, it is the reality described by the Schrödinger equation that forms the backdrop of the debate. Discussions of both reduction and emergence (weak or strong, ontological or epistemological) often confuse not only the differences between quantum and classical physics but also the real difficulties that arise in attempting to solve the Schrödinger equation for systems containing many particles. Clarifying how quantum mechanics can give directly accurate (exact) properties of materials is surely important if the scientifically informed debate is to progress, and we attempt to do so here by means of examples while making use of the bare minimum of mathematical formalism.<sup>1</sup>

Much of, in fact almost all of, chemistry could be considered an emergent property of the Schrödinger equation if the *chemical bond* is emergent, as this is one way to describe the properties of a material. In a basic course in chemistry one finds terms such as *covalent bond*, *ionic bond* and *metallic bonding*. A little further into the subject, and we come across terms such as *hydrogen bond*, *molecular bonding* and *van der Waals bond*. These alone give us insight into some of the properties of materials. Covalently bonded materials have a high melting point, are good thermal insulators, are bad electrical conductors and are brittle. In materials with metallic bonding, we observe a high melting temperature, good electrical and thermal conductivity and find the materials are ductile. Ionic bonds yield materials with a high melting point, good electrical insulation when solid but conducting well in the melt and so on. So given a description of bonding types, we immediately infer some bulk properties of materials.

There are, however, at least two problems with this approach. First, these concepts are purely qualitative and second, the definitions of such bonds are actually very badly defined: there are many (in fact, most) materials' bonding that is either intermediate between various pairs of these loosely defined categories or that have a mixture of these bonds. Additionally, one usually infers the type of bonding in a material from its properties, rather than the other way round. So the question arises: Given only fundamental principles of physics, can we do better? Can we find a model in which the chemical bond is a well-defined property rather than a conceptual one imposed after properties are known? Will other properties emerge from such formalism?

Yes: using quantum mechanics. However, it is only in recent years, with the onset of fast computers, advanced theory and algorithmic methods, that it has become possible to use quantum mechanics in such a quantitative manner to describe real materials.

### Non-relativistic quantum mechanics and Schrödinger's equation

First we will introduce enough basic quantum mechanics that we can demonstrate the practical problems in applying the formalism and how these can be obviated. We will then step through some examples to demonstrate emergent properties in real materials using only quantum mechanics; from simplicity, through complexity and back to emergent simplicity again.

The *wavefunction* of a material system, such as a solid, liquid or molecule, is a mathematical representation describing the potential results of a measurement on a system. Its square gives us a measure of the probability of finding particles in certain locations. If we have  $N$  particles (usually the electrons and atomic nuclei in a material) which are labelled with positions,  $r_1, r_2, \dots, r_N$  then the wavefunction is written in full as

$$|\Psi\rangle = |\Psi(r_1, r_2, \dots, r_N)\rangle,$$

that is, it is a function of all of the positions. Given that a macroscopic piece of material contains on the order of  $10^{26}$  atoms, it is immediately apparent that the wavefunction is a function in a huge number of dimensions. This high dimensionality is fundamentally the reason why solving its governing equation, the Schrödinger equation, computationally is far from trivial.

The Schrödinger equation describes the evolution of the wavefunction through time and is typically written

$$-i\frac{\partial}{\partial t}|\Psi\rangle = \hat{H}|\Psi\rangle,$$

or in a time-independent form

$$E|\Psi\rangle = \hat{H}|\Psi\rangle.$$

The left-hand side of this equation tells us how the wavefunction changes with time (in the time-dependent form) or the possible values of energy (in the time-independent form). The right-hand side describes the interactions of the particles and their surroundings. The symbol,  $\hat{H}$  known as the Hamiltonian of the system, consists of the sum of the kinetic energy (due to movement) and potential energy (due to interaction with other particles or with external fields). The operation of  $\hat{H}$  on  $|\Psi\rangle$  gives us the possible values of the total energy,  $E$ , of the system. The term  $-i\partial / \partial t$  is the time evolution operator. On the left side of the equation, the operation of this on the wavefunction gives us the rate of change of the wavefunction with time. Taken together, the Schrödinger equation tells us that the rate of change with time of the wavefunction at a given instant is related to the structure of the energy levels of the system.

More generally, a *measurement* on a system is mathematically described by an operator  $\hat{O}$  that acts on the wavefunction and gives us the result of the measurement and the likelihood of observing that result. That is, a given outcome of a measurement is indeterministic, with the probability of a possible outcome given by a weighting derived from the wavefunction.

The apparent simplicity of the Schrödinger equation is deceptive, concealing a number of snares. First, consider what is physically measurable in the Schrödinger equation. The two main “objects” in this equation are the energy and wavefunction, but neither of these are experimentally measurable quantities. Conversely, although time is experimentally measurable, there is no operator that acts on a wavefunction to give the time. There is therefore some disconnect between experimental measurement and the mathematical statement of the Schrödinger equation. Second, the number of dimensions in the wavefunction equals the number of degrees of freedom of the electrons. As noted earlier, macroscopic pieces of material contain on the order of  $10^{26}$  electrons, and it is simply not computationally feasible to handle such objects. That aside, we have to do some work on these objects to obtain the results of the experiment. In summary, the Schrödinger equation contains all the information needed to describe non-relativistic physical systems, but for realistic systems a full description in terms of equation is often analytically intractable as there is *too much* information. We will return to this point later.

As is common in problems involving many particles (including classical many-body problems), finding emergent properties often gives us insight into why things behave as they do that are not apparent from the constituent particles and their interactions. A simple analogy of emergent properties is seen by considering a flock of birds: if we take that a bird flies and introduce some simple rules (the behaviour of the flock causing individual birds to turn in a given direction, or climb, or dive, etc.), then the properties of the flock follows. We have something similar in the quantum system: the moving particles interact via a simple rule (Coulomb’s law). The Schrödinger equation is a shorthand mathematical formulation of these rules from which all material properties emerge.

## Solving the Schrödinger equation

In general, it is not yet possible to solve the Schrödinger equation in its entirety either analytically or computationally. However, a combination of recent theoretical and computational advances allows us to make considerable headway towards this and hence to determine emergent properties of materials. Here we will briefly mention the two methods required for solution: computer simulation (Clark et al. 2005) and density functional theory (Kohn and Sham 1965).

In simulation, one builds a model of a real system and uses it to explore the system. The model is mathematical, and the exploration is done using a computer, but in many ways simulations share the same goals as the experiment. However, in a simulation there is absolute control and access to detail, the ability to compute almost any observable quantity, and, given enough computer power, accurate answers for the model. Our model in the current case is the Schrödinger equation. This is vastly ambitious, because our goal is to model real systems using no approximations whatsoever.

Given unlimited computational power (both in memory and speed), the accurate, numerical solution to the full Schrödinger equation can be computed. However, we have relatively limited computational hardware, even with today's fastest supercomputers, and the solution of the Schrödinger equation is still many, many orders of magnitude away from being possible. The theoretical physics tool that we also need is *density functional theory* (DFT) which takes a remarkable approach to solving this complex mathematical and computational problem. DFT is both a profound, exact theory of interacting electrons and a practical prescription for calculating a solution. The idea is that it can be shown that the *wavefunction is not necessary* and we do not need to handle this huge-dimensional object. DFT says that this fundamental part of the Schrödinger equation can be bypassed and, instead, DFT aims to calculate the *electron density*, which is the probability of finding an electron at a particular point in space. This is a three-dimensional object, not a  $10^{26}$  dimensional object. DFT puts this electron density on a firm physical footing from a quantum mechanical point of view, and, from the electron density, we are able to define and calculate many emergent properties of materials using only fundamental ideas in quantum mechanics.

DFT tell us that when a system of interacting particles is in its lowest energy (ground) state, the density distribution of those particles in space uniquely determines the properties of the system. A functional (a function of a function) for the energy of the system can be written in terms of the density distribution that will determine the exact ground state density and energy. Therefore, a particular ground state energy and density distribution will be associated with a particular arrangement of atoms in the functional. The ground state density distribution will be that which globally minimises the energy functional, and the ground state energy will be that global minimum. Having bypassed the wavefunction and targeting the electron density directly means that we have reduced the dimensionality of our problem from  $\sim 10^{26}$  to 3. The problem is then computationally tractable. DFT therefore allows one to calculate the exact ground state properties of any interacting many-body object by transforming it into this more tractable system.

An important approximation that is made in most density functional calculations is known as the Born-Oppenheimer Approximation. In the limit where the masses of nuclei are much larger than the electron mass, it is possible to separate out the portion of the system that corresponds to the fast-moving electrons from that of the slow-moving atomic nuclei. This means that the behaviour of the electrons is only dependent on the positions of the ions, not their dynamics. We can then “clamp” the atoms in place while solving the Schrödinger equation for the electrons, and this will give us the ground state energy for that ionic configuration. Born-Oppenheimer is an excellent approximation for cases where nuclear motions are much slower than the rate at which electrons move. This is due to the large differences in electronic and nuclear masses, the nuclear mass being thousands of times larger than the electronic mass. Hence, for a given

instantaneous set of nuclear positions, the electrons will essentially always be in their lowest energy state. Therefore, in many cases, separating the degrees of freedom between electrons and nuclei is an incredibly good approximation.

Born–Oppenheimer allows us, for example, to compare the ground state energies of different static structural configurations with the same chemical formula and determine which is the most stable. Suppose that there are several possible stable molecular structures for a given set of ions. If we were to solve the Schrödinger equation for this collection, given arbitrary starting positions and away from the Born–Oppenheimer limit, we would find that we obtain a superposition of these stable molecular structures. By working in the Born–Oppenheimer limit, we have *selected* one of these structures. At first sight, this might seem to be an artificial, ad hoc intervention, but note that we have done nothing that nature does not itself do. In reality, the constituent ions would be interacting with the surrounding environment, and it is this interaction, which we have not so far considered, that would draw the nuclear wavefunction towards a form approximating that of the Born–Oppenheimer Approximation while realising one of the possible molecular structures. A close examination of the nature of this interaction between the molecular system and its environment is thus needed if emergentist accounts of molecular structure are to be sustained.

### Emergence of physical properties

Loosely speaking, many properties can “emerge” from the Schrödinger equation, some more easily than others. (One could ask if *all* properties of materials can be derived<sup>2</sup> from it.) In this section we detail a few interesting examples of properties seen to emerge from the Schrödinger equation using methods such as density functional theory.

*Pauli exclusion:* Before attempting to derive emergent properties from the Schrödinger equation, let’s examine an interesting property that we can obtain simply from the wavefunction. A fairly naïve, semi-classical picture of an atom is that of electrons in orbit around the nucleus – essentially a mini solar system. Unlike a solar system, the orbits are only allowed at particular distances (actually energies), and only one electron is allowed in the orbit (we’re ignoring a property called *spin* here, which complicates this argument without adding to the result). This property: *only one particle is allowed in each orbit* is called the *Pauli exclusion principle*. We will show that the less-than-obvious quantum result of the Pauli exclusion principle drops out of the wavefunction.

Electrons are indistinguishable, that is, you can’t tell one from another. If we have only two electrons in a system, its wavefunction can be written  $|\Psi(r_1, r_2)\rangle$ . If we swap the two electrons, then the wavefunction is  $|\Psi(r_2, r_1)\rangle$ . Now since electrons are indistinguishable, are these two wavefunctions equal? As noted earlier, we use operators on wavefunctions to make changes, so let’s call this swap  $\hat{S}$ . Mathematically we can write the description of swapping electrons as

$$\hat{S}|\Psi(r_1, r_2)\rangle = x|\Psi(r_2, r_1)\rangle.$$

We have inserted the unknown  $x$  here, as we don’t know if the swap changes the wavefunction. However, if we swap them back, then we return to where we started; two swaps restores the system to its original state, so we do know that

$$\hat{S}^2|\Psi(r_1, r_2)\rangle = 1|\Psi(r_1, r_2)\rangle$$

so we can immediately read off that  $\hat{S}^2 = 1$ , hence  $\hat{S} = \pm 1$ . Therefore, on swapping particles the wavefunction can do one of two things – remain unchanged ( $\hat{S} = 1$ ) or change sign ( $\hat{S} = -1$ ).

This gives us two classes of particles; the particles with  $\hat{S} = 1$  we call bosons and the particles with  $S = -1$  we call fermions. Electrons are in the second class of particles, where the wavefunction changes sign on swapping. Let's now attempt to put both electrons at the same position (call that position  $r$ ) so we know that on swapping them

$$|\Psi(r,r)\rangle = -|\Psi(r,r)\rangle$$

that is, when the particles are at the same place, then the wavefunction must be equal to negative itself. The only function that this holds for is zero, hence the probability of finding two fermions (for example, electrons) at the same place is zero. This is the Pauli exclusion principle, an emergent property, arising out of the wavefunction of a system that has no classical analogue. Returning to atoms, it is the exclusion property that determines the emergent orbital-like picture (essentially only one electron can exist in each “orbit”).

*Colour:* Why does a material have a particular colour? This is a straightforward question but with an answer deeply rooted in quantum mechanics. In isolated atoms, electrons occupy different energy levels. Due to the Pauli exclusion principle, it is only possible for electrons with different (up and down) *spins* to occupy the same energy level. In periodic, crystalline solids, these energy levels are replaced with bands of closely packed energy levels whose relative location and form are determined by the solution of the Schrödinger equation for that material. If an electron is excited from a filled level to an empty one by absorbing energy (usually a packet of light called a photon), then we have an electron in an *excited state*. However, not all photons are absorbed by the material, because electrons cannot absorb energies of arbitrary energies – electrons can only be in specific energy states. So to move an electron from one allowed state to another allowed state requires a photon whose energy is the difference in energy of those two states.

White light contains photons of all energies<sup>3</sup> in the visible spectrum. When this light shines on an object, it interacts with the electrons in the material. Photons with energies that correspond to the difference in electron energy levels get absorbed, and electrons are promoted from the lowest energy states to higher energy states. The remaining light is reflected from the object, and that is what reaches our eyes. The colour we see corresponds to the light that is not absorbed. For example, if light towards the red end of the spectrum (red, orange, yellow) is absorbed, then light towards the blue end is reflected, and that is the colour we see the object to be.

Hence the explanation of colour is quantum mechanical in nature; there is no classical description that explains colour. We can, in principle, solve the Schrödinger equation for an object and determine the energies of the electrons. The differences in these energies correspond to photon absorption, leaving non-absorbed photons to be reflected off of the object and some reach our eyes. Colour is an emergent property of the Schrödinger equation.

Of course one might ask, what happens to the energy of the absorbed photon? The electron which absorbs it can release the energy in a number of ways, the most common being transferring that energy to the kinetic energy of the atom – it makes the atom move or vibrate. The technical name for the quantum of motion of atoms in a material is a *phonon*. The kinetic energy of atoms is directly related to temperature. If the average kinetic energy of the atoms is given by  $E_{KE}$  then the temperature of the system is  $T \sim E_{KE}/k_B$  where  $k_B$  is known as Boltzmann's constant. The energy of absorbed photons gets translated into atomic motion and the material heats up. This is why darker materials (more light absorbed, less light reflected) get warmer than lighter-coloured materials.

The reverse of this process is also interesting. If we take a material and heat it up, then the kinetic energy of the atoms increases, and this energy can be transferred to the electrons and excite them into higher energy states. The electrons then fall back to their ground state and a



photon is emitted. This is the process that causes a material when heated to glow red, then as it gets hotter orange, and then white (all colours are emitted). Even hotter, such as in some stars, the peak of energy moves off to the high-energy end of the spectrum and the star is blue. This can all be determined from the Schrödinger equation, and so, closely related to colour is the emergent property of *temperature*.

*Chemical bonds:* It is normal for chemists to discuss the properties of materials derived from knowledge of their chemical bonding (Winter 1994). As described earlier, various bonding types exist: (i) *covalent* bonding where electrons are shared between pairs of neighbouring atoms which creates the intuitive “ball and stick” picture of atoms bonded into molecules and solids; (ii) *ionic* bonding where one atom gives up one or more (negative) electrons to another atom, leaving the donor atom positive and the receiving atom negatively charged. This allows the application of Coulomb’s law to explain attraction between the oppositely charged species; and (iii) *metallic* bonding, where some loosely bound electrons move in a negatively charged electron sea, held together by the positive ions. This electron sea is responsible for electrical conductivity.

Are these ideas of bonding emergent from the Schrödinger equation? Yes, but unfortunately in not such an elegant manner as the properties described earlier. The ideas of particular bonding types are somewhat idealised models and, in general, the electronic structure of materials doesn’t often lie fully within one bonding type, but is an incomplete mixture of bonding types. Let’s take the isolated atomic constituents of a material and solve the Schrödinger equation for each one of the isolated atoms. We then know what the wavefunction associated with each atom is and from this can construct a wavefunction associated with each electron in each one of the atoms. Let these wavefunctions be denoted by  $|\varphi_n\rangle$  where  $n$  labels each of the electronic states in each of the atoms. We can then express the solution to the Schrödinger equation of the solid or molecule in terms of these

$$|\Psi\rangle = \sum_n c_n |\varphi_n\rangle$$

where  $c_n$  is a number.<sup>4</sup> Loosely speaking, the square of the number  $c_n$  is the proportion of the electron density of the whole system that is found in atomic state  $|\varphi_n\rangle$ . We therefore know the equivalent atomic occupations that most closely resemble reconstructing the entire system from atomic orbitals. Using this, we can construct the number of electrons associated with each atom, and if we know the number of electrons on each atom, we know its charge and hence how *ionised* it is. This represents a direct measure of the strength of ionic bonds in the material.

For covalent bonds, instead of expressing the complete wavefunction as an expansion of atomic orbitals, we express it as an expansion of orbitals that represent sharing between pairs of atoms. We then know the amount, directionality and occupation of covalent bonding in the material. Metallic bonding also proceeds similarly, but with the complication that states localised around atoms are found to be partially occupied, containing, on average, fractions of electrons. This is because some of the electronic charge is smeared out over the entire material representing the metallic sea of electrons that essentially form the metallic behaviour.

In realistic systems, when one evaluates the wavefunction and expresses it in the earlier form, it is usual to find that such idealised pictures of covalent, ionic or metallic bonding individually don’t represent the electron density. This is because in real systems bonding tends to be a mixture of these different types, and one has to say, for example, a bond is partially ionic and partially covalent. The emergent picture of bonds becomes less clear when we start to classify how much of different types of bonds form the bonds in a material. We end with classifications such as strongly covalent, weakly ionic, semi-metallic and semiconducting, to name a few. These can all be classified by the proportions of types of bond in the material (and also using the energy difference between the ground state of the system and the energy of the first excited state).



Bonding might appear a somewhat artificial emergent property derived from the Schrödinger equation. However, there are some fundamental reasons why such bonding forms a good viewpoint of the electronic structure of materials and leads to the deeper and qualitative understanding of their properties. Quantum mechanics tells us that electrons being shared between atoms, or transferred from one atom to another, can reduce the energy. This is because the lowest energy state of atoms is one in which electrons pack in a certain order. By forming materials by grouping large numbers of atoms, the electrons still try to form the lowest energy states by sharing themselves or moving between atoms, and the manner in which they do this (transferring/sharing) is exactly what we call a chemical bond. So in essence, a chemical bonding is a consequence of the Schrödinger equation and hence an emergent property of it, and these bonds allows us a simple but powerful picture of materials at the atomic level.

*Phonons:* In a material the constituent atoms have kinetic energy, which are directly related to the temperature of the material. Once a regular crystal structure has been made, quantised lattice vibrations called phonons (Born and Huang 1954) may be excited in it. The mechanism is analogous to a vibrating string; specific vibrational frequencies are allowed. Phonons, which are a collective excitation of atomic positions, play an important role in the thermal properties of material properties, since they conduct heat alongside electrons, and also play an important role in the formation of Cooper pairs in the BCS theory of superconductivity (Bardeen et al. 1957).

We can obtain phonons from the Schrödinger equation. Starting from a very simple case we can build up the picture. A mass hanging on a spring will vibrate at a given frequency, and the stiffer the spring, the higher the vibrational frequency. Similarly, a taut string will vibrate at a given frequency, and the more the tension on the string, the higher the frequency. Let the mass or string extend from its equilibrium length by an amount,  $x$ , and let the tension in the string or strength of the spring be  $k$ . Then the energy and displacement are related by Hooke's law  $E = \frac{1}{2}kx^2$ . The second derivative of this equation with respect to  $x$  gives us  $k$ , thus  $k = d^2E / dx^2$ .

Returning to the atomic systems of materials, the Schrödinger equation gives us the energy,  $E$  and  $x$  represents the displacements of atoms from their equilibrium sites under excitation of atomic vibrations. It is a technicality to take the second derivative of the Schrödinger equation and a complex computational task to solve such an equation, but within density functional theory this has been done (Refson et al. 2006), and essentially the spring constants  $k$  can be evaluated. The vibrational frequencies are given by  $\omega = \sqrt{k/m}$  where  $m$  is atomic mass. So atomic vibrations can be evaluated from the Schrödinger equation, leading to thermodynamic quantities (Kittel and Kroemer 1980) such as vibrational entropy or Gibbs free energy.

Higher-order derivatives can also be calculated which go beyond what is known as the harmonic approximation and leads to temperature-dependent quantities such as thermal expansion, thermal conductivity and spectroscopic features such as those of Raman spectroscopy. Therefore, temperature, heat and thermodynamic properties of materials are emergent from the Schrödinger equation.

*Magnetism:* In the previous discussion we mentioned one of the properties of fundamental particles such as electrons. It is known as the spin and has units of angular momentum. To get some insight as to what this is, let's return to the solar system cartoon of the atom. In this picture, an electron's orbit of the atomic nucleus would represent the "year" (a planet orbiting a star, one planet-year is the time taken for one orbit). The spin can be thought of as the "day", the time for the object to rotate on its axis once. As all electrons are indistinguishable, the "day" is a particular value; essentially the electron carries a fixed, intrinsic value of angular momentum that we call its spin (for an electron this value of angular momentum is  $\hbar/2$  where  $\hbar$  is Planck's constant as found in the Schrödinger equation; it is the quantised, fundamental unit of angular momentum).

Angular momentum is a vector quantity, which means it points in a given direction. The electron spin pointing in a certain direction is the basis for magnetism; the electron carries a magnetic field, with a north pole and a south pole. In many materials electrons tend to pair up with one electron having its spin pointing in one direction (often called spin-up) and the other pointing in the opposite direction (spin-down). Such materials are generally called non-magnetic, as the magnetic fields from the electron spins exactly cancel. However, in some materials, the lowest energy configuration occurs when the spins on the electrons are not all equally paired up, leaving a net local electron spin. These are commonly described as *magnetic materials*. Can we get this from the Schrödinger equation? Yes, but we have to be more precise with our language and concept of a wavefunction: the wavefunction is not a function of just the positions of the electrons but also their spin:

$$|\Psi\rangle = |\Psi(r_1, s_1, r_2, s_2, \dots, r_N, s_N)\rangle,$$

where  $s$  labels the spin on the electrons. The Schrödinger equation becomes more complicated to solve, but the principle of emergent quantities that can be obtained from it still holds.

The magnetic properties of a material arise from the interaction of many spins located on ions composing the crystal lattice of the material. We can define an exchange constant  $J$  along pathways between pairs of neighbouring spins, which is the energy needed to flip one spin into the opposite direction. We use the solution of the Schrödinger equation (often in the form of density functional theory) to calculate the relative energies of spin configurations, which allow us to directly calculate the spin-flipping  $J$  energies. These allow us to build a model of a magnetic material with spins being placed at regular lattices. This is known as an *Ising model* for the case where the spins are only allowed to take two directions, up and down. For so-called Heisenberg systems, the spins are allowed to rotate in any direction in space, but the principle is the same. This allows us to state a very simple, but very powerful, model of magnetism:

$$E = J \sum_{\{i,j\}} \underline{s}_i \cdot \underline{s}_j$$

where the sum is over pairs of neighbouring spins. We can then introduce temperature and obtain the temperatures at which various spin configurations occur. Although we have only introduced a simple, idealised model, it is used only by way of example to illustrate how magnetic properties emerge from non-relativistic quantum mechanics. Such models can be made more detailed and used to obtain significant insight into the other emergent properties of magnetic materials (Landau 1969).

## Conclusions

We have outlined a minimum number of concepts in quantum mechanics, allowing a description of sample emergent properties. Although some concepts in quantum mechanics arise in a probabilistic manner, it does not follow that all properties are probabilistic. A large number of material properties exist that follow directly from the Schrödinger equation that are definite in value. Although the locations of electrons in a material can only be determined with a probability, the properties of materials are often determined not by the location of electrons but by their energy. The Schrödinger equation gives us energies which give rise directly to properties such as colour, temperature and magnetism. Even given the probabilistic nature of the position of electrons, we can evaluate types of bonding, which gives us great insight into properties of materials.

Finally, we conclude with some speculation. We have demonstrated that starting from nuclei, electrons and their interactions, we are able to obtain properties of materials that are not properties of the “parts”. These are emergent properties, and we would likely call this “weak” emergence. However, we are not aware of any properties that have been *demonstrated* to be emergent in any other sense, which we could call “strongly” emergent. Are there any (non-relativistic) properties of materials that cannot be obtained from solving the Schrödinger equation? Essentially, how likely is the reductionist point of view of the world? Here we have described a small number of properties but could have included electrical conductivity, melting points, mechanical strength, viscosity, speed of sound in a material, specific heat and so on. So what can we not get, and are there any “strongly” emergent properties? There is much debate on this, but we note that, historically, as soon as we discover a mechanism of how a particular property of a material works in the quantum mechanical realm, we quickly find out how to extract it from the Schrödinger equation. An interesting example is superconductivity. A mechanism for superconductivity was discovered in the 1950s (the BCS mechanism), which involved electrons and phonons coupling together. That allowed the calculation of superconducting properties such as transition temperatures. In the 1980s a new and different class of superconductivity was discovered (called high- $T_c$  superconductivity). The mechanism for this remains unknown, but is it hidden in the Schrödinger equation? Probably.

### Notes

- 1 It is useful to highlight the acute disjunction between the classical and quantum depictions of the world around us. Conceptually, the quantum realm is quite alien compared to the domain of classical physics: notions such as entanglement and non-locality have no clear equivalents in classical mechanics, and discussions of reduction and emergence must, if they are to take science seriously, avoid simply assuming that there is no real difference between the two. There is no interpretation of quantum mechanics in which all the weirdness “goes away” – at best, one only replaces one kind with another.
- 2 There is some debate (Clark 2017) as to whether this is the case and whether some properties of materials are not derivable properties of a quantum treatment of systems, causing debates on top-down versus bottom-up causation and divisions into definitions of strong and weak emergence.
- 3 The energy of a photon determines many of its properties. For example, if a photon has an energy,  $E$ , it has a frequency,  $f$ , related by  $E = hf$ , where  $h$  is known as Planck’s constant. If  $c$  is the speed of light, then the wavelength,  $\lambda$ , of the photon is given by  $\lambda = c/f$ .
- 4 Note that there are different ways to combine these single electron states that add unnecessary detail to this picture, so we will, without loss of generality, continue with this straightforward combination.

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