PH320: Condensed Matter Physics II

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LECTURE NOTES

1 Hamiltonian, symmetries and models (2 Lectures)

- Throughout the course we shall work in three spatial dimensions unless otherwise stated.
- Question: If we wish to study an aggregate of N atoms (enclosed in a volume V) what is the minimal system we need to consider? What are the important degrees of freedom?
- Consider this: Each of the N atoms have z valance electrons (the core electrons do not participate in the physics that we are interested in...in some sense the same way as we not interested in quarks that make up the nucleons in the nuclei).
- Key degrees of freedom: The positions and momenta $(\mathbf{R}_I, \mathbf{P}_I)$ of the N ions whose mass is M, and the positions and momenta $(\mathbf{r}_i, \mathbf{p}_i)$ of the $N_e = zN$ valance electrons whose mass is m (we will drop the "valance" adjective from now on). We will put in the spin degrees later on.
- Note that this is the first step in most of physics research: Find out the degrees of freedom or Hilbert space of the physical system we wish to study.
- Next, we need to state its hamiltonian
- The hamiltonian in our context will contain many things, notably
  1. Kinetic energy of ions
  2. Kinetic energy of electrons
  3. Coulomb interaction energy between ions
  4. Coulomb interaction between ions and electrons
  5. Coulomb interaction between electrons and electrons
  6. Spin orbit interaction
  7. Hyperfine interaction
  8. etc...
  9. Muck (aka disorder), stuff that you did not want...or even added intentionally
  10. and...any potentials or fields that *you* have applied!
- Lets put down an equation for the hamiltonian (keeping first five terms that we mentioned)

$$\mathcal{H} = \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M} + \sum_{i=1}^{N_e} \frac{\mathbf{p}_i^2}{2m} + \frac{z^2 e^2}{4\pi\epsilon_0} \sum_{\langle IJ \rangle} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|} - \frac{z e^2}{4\pi\epsilon_0} \sum_{\langle Ij \rangle} \frac{1}{|\mathbf{R}_I - \mathbf{r}_j|} + \frac{e^2}{4\pi\epsilon_0} \sum_{\langle ij \rangle} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (1.1)$$

where $\langle\rangle$ runs over all pairs. (☞ Actually, this is not all so good as it seems...one can put down a "better" hamiltonian. Criticize this hamiltonian, and state your "better" version.)

- There are many other operators that we define on the Hilbert space that represent physical quantities that we are interested in. For example, we can write an operator for electron current $\mathbf{J}$. (☞ What is the expression for $\mathbf{J}$?)
- Our system is kept at a temperature T.
- We want predict the outcome of an experimental measurement of an operator O. What should we do?
- Very easy (... to *state*)
  1. Diagonalize the hamiltonian aka find all eigenvalues and eigenfunctions
  $$\mathcal{H}|\Psi_n\rangle = E_n|\Psi_n\rangle \tag{1.2}$$
  2. We know in equilibrium, the system have a thermal Boltzmann distribution, thus
  $$\langle O\rangle = \frac{\sum_n e^{-\beta E_n}\langle\Psi_n|O|\Psi_n\rangle}{\sum_n e^{-\beta E_n}} \tag{1.3}$$
  where $\beta = 1/T$ (we measure temperature in *energy* units so that $k_B = 1$). Make sure that you understand the meaning of the equation clearly and thoroughly.

  ...but *very hard* (if not impossible) to do! Thus writing down the hamiltonian eqn. (1.1) only helped us practise our LaTeX skills and admire the outcome!
- It appears that we are staring at defeat...even before we started! What should we do?
- Forced to simplify...how to simplify?
- What do we really mean by "simplify"? Make a model that is (at least approximately) tractable, but *provides for the essential physics* of the problem at hand.
- Guiding principles of simplification
  - Symmetries
  - Scales

1.1 Symmetries

- What is a symmetry operation? A symmetry operation is a transformation (something that we can perform on the Hilbert space) that leaves *the (absolute) value of the inner product of any two states invariant.*

  Obviously, this leaves the lengths of all vectors invariant.
- Stated in equations: If $\mathcal{U}$ is a symmetry operation, then for every vector $|\psi\rangle$ of my Hilbert space, there is a new vector $|\psi'\rangle = \mathcal{U}(|\psi\rangle)$. The map $\mathcal{U}$ is such that it satisfies
  $$|\langle\phi'|\psi'\rangle| = |\langle\phi|\psi\rangle| \tag{1.4}$$
  for any two vectors $|\psi\rangle$ and $|\phi\rangle$.

- Note that at this stage of discussion, $\mathcal{U}$ is a map from the Hilbert space to itself. The natural question: what kind of a map is it? Can we write a general formula for such maps?

- WEIGNER (in 1930s shortly after QM was discovered) showed that a symmetry transformation has to be *either a linear or an anti-linear* operator – this is called Weigner's theorem (we shall not prove it here).

- Written out in equations, $\mathcal{U}$ is either a *linear operator*, i. e.,

  $$\mathcal{U}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha\mathcal{U}|\psi\rangle + \beta\mathcal{U}|\phi\rangle \tag{1.5}$$

  or an *anti-linear* operator which means

  $$\mathcal{U}(\alpha|\psi\rangle + \beta|\phi\rangle) = \alpha^*\mathcal{U}|\psi\rangle + \beta^*\mathcal{U}|\phi\rangle \tag{1.6}$$

  where the $*$ denotes complex conjugation. Surely you have seen linear operators prior to this. Likely that you may not have seen anti-linear operators yet. So please take a moment to understand what an anti-linear operator is – understand the definition clearly. (☞ If you are keen, try this: Consider the vector space $\mathbb{C}$, and find an anti-linear operator on this.)

- We ask: Given a symmetry operation, *is it a symmetry of our system?* Recall that our system is the given Hilbert space *and* the hamiltonian.

- A given symmetry operation describes a symmetry of our system if it satisfies

  $$\mathcal{U}^{-1}\mathcal{H}\mathcal{U} = \mathcal{H} \tag{1.7}$$

  Stated in English, if the hamiltonian is invariant under the symmetry operation, then such a symmetry operation describes a symmetry.

- If $\mathcal{U}$ is a symmetry of our system, and if $|\Psi\rangle$ is an energy eigenstate with eigenvalue E, i. e., $\mathcal{H}|\Psi\rangle = E|\Psi\rangle$, then it follows that the state $\mathcal{U}|\Psi\rangle$ is also an eigenstate of $\mathcal{H}$ with the same energy eigenvalue.

- Let us discuss the symmetries of our atom-aggregate system. Here are the usual suspects: translation, rotation etc.

- Translation:
  - This symmetry is described by a *linear* operator $\mathcal{T}$
  - One can translate the system by any amount $\mathbf{a}$ one wishes...i. e., $\mathcal{T}$ depends on $\mathbf{a}$, we write $\mathcal{T}(\mathbf{a})$.
  - Clearly, $\mathcal{T}(\mathbf{a}+\mathbf{b}) = \mathcal{T}(\mathbf{a})\mathcal{T}(\mathbf{b}) = \mathcal{T}(\mathbf{b})\mathcal{T}(\mathbf{a})$
  - What about translating by $\mathbf{0}$? $\mathcal{T}(\mathbf{0}) = \mathcal{I}$...this is the identity operator on the Hilbert space.
  - Also $\mathcal{T}(-\mathbf{a}) = \mathcal{T}^{-1}(\mathbf{a})$

  One can see that the *set of all* translations form an Abelian group. (☞ Do the same for rotations. How do we describe rotations? Do the set of all rotations form a group? If yes, is it Abelian?)

- Note that translations are described by a continuous parameter...hence translation is called a *continuous symmetry*. So are rotations. Our system can have discrete symmetries as well (we will see this soon).

- We need two math results:

  1. One can show that if the symmetry ($\mathcal{U}$) is described by a linear operator, eqn. (1.4) implies that $\mathcal{U}$ is *unitary*.
  2. Another beautiful result: every unitary operator $\mathcal{U}$ can be written as $e^{i\mathcal{W}}$ where $\mathcal{W}$ is a *Hermitian operator*.

- Now what is the $\mathcal{W}$ that corresponds to $\mathcal{T}(\mathbf{a})$...we know this from basic quantum mechanics...this is the related to the momentum operator

$$\mathcal{T}(\mathbf{a}) = e^{-i\frac{\mathbf{a}\cdot\mathcal{P}}{\hbar}} \tag{1.8}$$

  where $\mathcal{P}$ is the *total* momentum operator.

- Note that the statements "$\mathcal{T}(\mathbf{a})$ is a symmetry" and "$\mathcal{P}$ is a conserved quantity" are equivalent. We say that momentum is the generator of translations.

- This is a very generic feature (Noether's theorem): Associated with every continuous symmetry, there is a conserved quantity. (☞ What is the conserved quantity associated with rotations?)

- Lets turn things around a bit. Can we now start with a conserved quantity and "discover" a symmetry?

- Most interestingly, in addition to the usual suspects, there is a conserved quantity that we do not usually see explicitly in elementary courses. Our hamiltonian actually conserves the number of particles (ions + electrons, in fact, *separately*; we will not go into this now) – call the operator that counts the number of particles as $\mathcal{N}$ ($[\mathcal{N}, \mathcal{H}] = 0$).

- Define $\mathcal{G}(\theta) = e^{-i\theta\mathcal{N}}$ and indeed this is a symmetry of our hamiltonian. This is called the "global phase" or "global gauge" symmetry. It may not be evident at this point why this is important; you will have to wait a while to see where this will become important. (☞ Do $\mathcal{G}(\theta)$ form a group? If yes, have you seen this group before?)

- All symmetries considered so far are continuous. There are many important discrete symmetries; in particular, there is one that we will discuss in detail.

- This is the so called "time reversal" symmetry – turns out to be crucially important.

- The key ideas behind time reversal are two:

  - The idea of a time reversed state.
  - The idea of a reverse time evolution.

  Let us illustrate the two ideas first in the simplest *classical* case.

- Consider a classical particle – its state is a point $\mathbf{s}$ in the phase space described by two vectors $(\mathbf{r}, \mathbf{p})$. The "time reversed" partner of this state is the one given by $\boldsymbol{\Theta}\mathbf{s} = (\mathbf{r}, -\mathbf{p})$ - we have introduced here the formal time reversal operator $\boldsymbol{\Theta}$. Note carefully what happens – in the time reversal operation, the position is unchanged and the momentum changes to the *opposite* direction. (☞ Consider a particle on a ring. What is a generic state of the particle? Write its time reversed state.)

- Note that $\mathbf{\Theta}^2$ is the identity on this classical system.
- The second idea: Reverse time evolution is when you integrate the hamiltonian equations (for this you will use the given hamiltonian $\mathcal{H}(\mathbf{r},\mathbf{p})$) in negative time. That is you start at time $t = 0$ and go to a time $t = -t_{end}$. This is to be compared with what is usually done: Start time at $t = 0$ and end at $t = t_{end}$.
- Consider the initial state $\mathbf{s}_i$ at time $t = 0$. After the usual time evolution this state becomes $\mathbf{s}_f$ at time $t = t_{end}$. Let us denote this symbolically,

  $$\mathbf{s}_f = E_{\mathcal{H}}(t_{end})\mathbf{s}_i \tag{1.9}$$

  where $E_{\mathcal{H}}(t_{end})$ stands for the process of integrating the equations from $t = 0$ to $t = t_{end}$.
- Now consider this. At $t = 0$ start with the time reversed state $\mathbf{\Theta s}_i$. Evolve this by the hamiltonian $\mathcal{H}$ to a negative time i. e., $t = -t_{end}$ we will obtain some state $\mathbf{s}'_f$. In math,

  $$\mathbf{s}'_f = E_{\mathcal{H}}(-t_{end})(\mathbf{\Theta s}_i) \tag{1.10}$$

- The key question: What is the relationship between $\mathbf{s}_f$ and $\mathbf{s}'_f$? In particular is $\mathbf{\Theta s}_f \underbrace{=}_{?} \mathbf{s}'_f$?
- Here is the statement: If $\mathbf{\Theta s}_f = \mathbf{s}'_f$ for all $\mathbf{s}_i$ and t_{end} then we say that the hamiltonian (i. e., the system) is *time reversal symmetric*. We can easily see what this means by means of a simple harmonic and a damped simple harmonic oscillator.
- Allow me to state this again: In a system with time reversal symmetry the state obtained by reverse time evolution of time reversed initial state is always same as the time reversed final state obtained by forward time evolution of the initial state.
- Now let us see what we should do in quantum mechanics. Let us form here on denote $\mathbf{\Theta}$ as the time reversal operator on our Hilbert space.
- First is the idea of a time reversed state. Consider a Hilbert space of a single spinless particle. Very reasonable for even unreasonable people:

  $$\mathbf{\Theta}|\mathbf{r}\rangle = |\mathbf{r}\rangle \tag{1.11}$$
  $$\mathbf{\Theta}|\mathbf{p}\rangle = |-\mathbf{p}\rangle \tag{1.12}$$

  Thus if a particle is in an eigenstate of position operator, it is invariant under time reversal. If it is in a momentum eigenstate, the time reversed state corresponds to the momentum eigenstate with opposite momentum. Compare this with the classical case. You will see that it is quite consistent.
- Start from the state $|\psi_i\rangle$ and perform the time evolution to t_{end}; we get $|\psi_f\rangle = S(t_{end})|\psi_i\rangle$ where $S(t_{end}) = e^{-i\frac{\mathcal{H}t_{end}}{\hbar}}$
- Let us now start with $|\psi'_i\rangle = \mathbf{\Theta}|\psi_i\rangle$, i. e., the time reversed state. Perform the reverse time evolution to get $|\psi'_f\rangle = S(-t_{end})\mathbf{\Theta}|\psi_i\rangle$.
- Again we ask $\mathbf{\Theta}|\psi_f\rangle \underbrace{=}_{?} |\psi'_f\rangle$? If they are equal, for all $|\psi_i\rangle$ and t_{end}, then we say that the hamiltonian (our system) has time reversal symmetry.

- Suppose that the given hamiltonian $\mathcal{H}$ is time reversal symmetric. Then we have

  $$\boldsymbol{\Theta} e^{-i\frac{\mathcal{H}t}{\hbar}} = e^{i\frac{\mathcal{H}t}{\hbar}} \boldsymbol{\Theta} \tag{1.13}$$

  which reduces to (☞ how?)

  $$\boldsymbol{\Theta}(-i\mathcal{H}) = i\mathcal{H}\boldsymbol{\Theta} \tag{1.14}$$

- The temptation to conclude

  $$\boldsymbol{\Theta}\mathcal{H} + \mathcal{H}\boldsymbol{\Theta} = \{\boldsymbol{\Theta}, \mathcal{H}\} = 0 \tag{1.15}$$

  is very strong...so let us succumb to it.

- We will now discover that for a free particle this conclusion leads to absurd results. For a free particle $|\mathbf{p}\rangle$ is an eigenvalue of the hamiltonian with energy $\frac{p^2}{2m}$. Using eqn. (1.15) we are forced to conclude that $\boldsymbol{\Theta}|\mathbf{p}\rangle$ is a state whose energy is $-\frac{p^2}{2m}$ which is manifestly absurd since the kinetic energy of the free particle cannot be negative. Our conclusion of eqn. (1.15) from eqn. (1.14) is therefore incorrect. In fact in making this wrong conclusion, we tacitly assumed that $\boldsymbol{\Theta}$ is a linear operator. The moral of this calculation is that $\boldsymbol{\Theta}$ *cannot* be a linear operator!

- The other possibility is that $\boldsymbol{\Theta}$ is an *anti-linear* operator. Now the LHS of eqn. (1.14) will pick up a negative sign when we pull out the i to the left of $\boldsymbol{\Theta}$, and we get

  $$\boldsymbol{\Theta}\mathcal{H} - \mathcal{H}\boldsymbol{\Theta} = [\boldsymbol{\Theta}, \mathcal{H}] = 0 \tag{1.16}$$

  Thus, *time reversal operator is an anti-linear operator that commutes with the hamiltonian.* (☞ Show that the free particle case discussed above works out nicely.)

- We will like to write $\boldsymbol{\Theta}$ in a form similar to eqn. (1.8). Let us explore.

- We first ask how do the standard operators (for a particle) change under time reversal transformation. Clearly

  $$\boldsymbol{\Theta}^{-1}\mathbf{r}\boldsymbol{\Theta} = \mathbf{r} \tag{1.17}$$

  $$\boldsymbol{\Theta}^{-1}\mathbf{p}\boldsymbol{\Theta} = -\mathbf{p} \tag{1.18}$$

  $$\boldsymbol{\Theta}^{-1}\mathbf{L}\boldsymbol{\Theta} = -\mathbf{L} \tag{1.19}$$

  ($\mathbf{L}$ is angular momentum), these are simply restatement in quantum language what we know from classical mechanics.

- Consider (for a spinless particle) in a state $|\psi\rangle$. What is the time reversed state $\boldsymbol{\Theta}|\psi\rangle$? Let us try to understand in component language...

  $$\begin{aligned} |\psi\rangle &= \int d\mathbf{r}\, \psi(\mathbf{r})|\mathbf{r}\rangle \\ \Rightarrow \boldsymbol{\Theta}|\psi\rangle &= \int d\mathbf{r}\, \psi^*(\mathbf{r})|\mathbf{r}\rangle \end{aligned} \tag{1.20}$$

  where we have used eqn. (1.11). Aha, now we see it...the time reversed state whose wavefunction is $\psi(\mathbf{r})$ has the wavefunction $\psi^*(\mathbf{r})$! Looks like time reversal operator is best discussed in component form.

- Let $|\phi'\rangle = \boldsymbol{\Theta}|\phi\rangle$ and $|\psi'\rangle = \boldsymbol{\Theta}|\psi\rangle$. You can go on to show that $\langle\phi'|\psi'\rangle = (\langle\phi|\psi\rangle)^*$, and due to this timereversal is often called antiunitary.

- We are in a position to state our first non-trivial result. The eigenstate of a time reversal invariant hamiltonian (of our spinless particle), if non-degenerate, has a wavefunction that an be chosen to be real. (☞ Actually, the result applies also to a collection of spinless bosons.)

- There is also one more interesting thing that we find for a spinless particle: $\boldsymbol{\Theta}^2 = \mathcal{I}$ (☞ Show this. Does this mean that $\boldsymbol{\Theta}^{-1} = \boldsymbol{\Theta}$?)

- You might now legitimately ask: But this course is about electrons in materials, and electrons are not spinless! How does time reversal work on particles with spin?

- Let us consider the spin operator $\mathbf{S}$, its components satisfy

  $$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k \tag{1.21}$$

  We expect, and it is true, that

  $$\boldsymbol{\Theta}^{-1}\mathbf{S}\boldsymbol{\Theta} = -\mathbf{S} \tag{1.22}$$

  (☞ What happens to the commutation relation?)

- We will now require a mathematical statement to move forward (we try to avoid as much formal mathematics as we can, but it is necessary here). The statement is the following. Every antiunitary operator is a composition of the "complex conjugation operator" and a unitary operator. Applying this theorem to our time reversal operator we get

  $$\boldsymbol{\Theta} = UK \tag{1.23}$$

  where K is the complex conjugation operator and U is the unitary operator. We will now understand what this means by going back to the spinless particle.

- What is the complex conjugation operator? It turns out that the most painless way to develop this is to use a basis set for our system. Let us say this is $|m\rangle$. Then any state of our system can be written as $|\psi\rangle = \sum_m \psi(m)|m\rangle$. We have

  $$K|\psi\rangle = \sum_m \psi^*(m)K|m\rangle = \sum_m \psi^*(m)|m\rangle \tag{1.24}$$

  We *take* that the complex conjugate operation does nothing on the base kets. Naturally if I choose another basis, I will find that K has a different behaviour on the state $|m\rangle$. But it all works out since the "change in K" will be compensated by a "change in U", so that $\boldsymbol{\Theta}$ is basis independent. Moral: K and U depend on the choice of the basis, once the basis is chosen the action of K on a state is given by eqn. (1.24).

- Next question: What is U? We know U is a unitary (and therefore *linear*) operator. Follow this

  $$\boldsymbol{\Theta}|\psi\rangle = UK|\psi\rangle = U\sum_m \psi^*(m)|m\rangle = \sum_m \psi^*(m)U|m\rangle \tag{1.25}$$

  What is now evident is that if I specify the action of U on the basis kets $|m\rangle$, I am done!

- Based on the discussion above we now see that the action of the unitary operator on the basis vectors *has* to be basis dependent (since K is basis dependent). Let us choose the position basis of our spinless particle – we need $\mathsf{U}|\mathbf{r}\rangle$. What is it? Obvious: $\mathsf{U}|\mathbf{r}\rangle = |\mathbf{r}\rangle$, thus for the position basis U is the identity operator! One now recovers eqn. (1.20). What happens if we use the momentum basis? Well $\mathsf{U}|\mathbf{p}\rangle = |-\mathbf{p}\rangle$, and clearly U in this basis is *not* the identity! (☞ Show that everything is consistent, i. e., show that $\boldsymbol{\Theta}|\psi\rangle$ obtained by using either (position or momentum) basis is the same).

- We are now ready to tackle the spin-$\frac{1}{2}$ particle. The general state of a spin-$\frac{1}{2}$ particle can be written in position basis as

$$|\psi\rangle = \sum_{\sigma} \int d\mathbf{r}\, \psi_{\sigma}(\mathbf{r})\, |\mathbf{r}\sigma\rangle \tag{1.26}$$

  where $\psi_{\sigma}(\mathbf{r})$ is the two-component Pauli spinor wavefunction; yes, $\sigma = \uparrow, \downarrow$.

- We know what happens to the spatial ("orbtial") part under time reversal, so let us focus on the "spin part" – a general spin state can be written as

$$|\psi\rangle = \psi_{\uparrow}|\uparrow\rangle + \psi_{\downarrow}|\downarrow\rangle = \sum_{\sigma} \psi_{\sigma}\, |\sigma\rangle \tag{1.27}$$

  where $|\sigma\rangle$ are the eigenstates of the S_z operator for some chosen z-direction.

- Okay, enough with the linguistics... we ask what is $\boldsymbol{\Theta}|\psi\rangle$? We have

$$\begin{aligned} \boldsymbol{\Theta}|\psi\rangle &= \sum_{\sigma} \psi^{*}_{\sigma}\boldsymbol{\Theta}|\sigma\rangle \\ \Rightarrow \mathsf{U}\mathsf{K}|\psi\rangle &= \sum_{\sigma} \psi^{*}_{\sigma}\mathsf{U}|\sigma\rangle \end{aligned} \tag{1.28}$$

  We, therefore, need the action of the unitary operator U on the spin up and down eigenstates.

- What could $\boldsymbol{\Theta}|\sigma\rangle = \mathsf{U}|\sigma\rangle$ be? What *should* it be? Here is the logic
  - $\boldsymbol{\Theta}|\uparrow\rangle$ should be parallel to $|\downarrow\rangle$ and $\boldsymbol{\Theta}|\downarrow\rangle$ should be along $|\uparrow\rangle$...this is our intuition.
  - Since U is unitary, and therefore there is some Hermitian $\mathcal{W}$ such that $\mathsf{U} = e^{i\mathcal{W}}$.

  So if we are able to find a Hermitian $\mathcal{W}$ such that up-state maps to something parallel the downstate and the downstate maps to something parallel to the upstate we are done!

- Can we find such a $\mathcal{W}$? Yes, of course! Think of rotation about the y-axis by an amount π, we get

$$\mathsf{U} = e^{-i\frac{\pi S_y}{\hbar}} \tag{1.29}$$

  a formula that is applicable to *any spin* (not just $\frac{1}{2}$) (☞ Show this.)

- For our spin $\frac{1}{2}$ system, we get

$$\mathsf{U} = e^{-i\frac{\pi S_y}{\hbar}} = e^{-i\frac{\pi\sigma_y}{2}} = -i\sigma_y = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \tag{1.30}$$

  where σ_y is a Pauli matrix.

- So what is $\boldsymbol{\Theta}|\uparrow\rangle$; this is equal to $U|\uparrow\rangle = |\downarrow\rangle$...this is as expected...great! What about $\boldsymbol{\Theta}|\downarrow\rangle$? Well, this is equal $U|\downarrow\rangle = -|\uparrow\rangle$...hmm...we get a minus sign!

- Now what is $\boldsymbol{\Theta}^2|\uparrow\rangle$...this is $-|\uparrow\rangle$! This happends for $\downarrow$ state as well; $\boldsymbol{\Theta}^2|\downarrow\rangle = -|\downarrow\rangle$! Well, it appears that $\boldsymbol{\Theta}^2 = -\mathcal{I}$...we are now panicking!

- Lets check out the action of $\boldsymbol{\Theta}^2$ on any spin state:

  $$\boldsymbol{\Theta}^2|\psi\rangle = \boldsymbol{\Theta}\left(\sum_\sigma \psi^*_\sigma \sigma|\bar{\sigma}\rangle\right) = \sum_\sigma \psi_\sigma \sigma\bar{\sigma}|\sigma\rangle = -|\psi\rangle \tag{1.31}$$

  ($\bar{\sigma} = -\sigma$) which now confirms indeed that $\boldsymbol{\Theta}^2 = -\mathcal{I}$!! Note that this is a peculiarity of *half integral spins*, for even integral spins this (such as spin zero), we will not get the negative sign. This is quantum mechanics showing is true prowess...*nothing* like this ever appears in classical mechanics.

- If we now put the orbital part back in, we can summarize the effect of $\boldsymbol{\Theta}$ on the basis vectors as

  $$\begin{align} \boldsymbol{\Theta}|\mathbf{r}\sigma\rangle &= \sigma|\mathbf{r}\bar{\sigma}\rangle \tag{1.32} \\ \boldsymbol{\Theta}|\mathbf{p}\sigma\rangle &= \sigma|-\mathbf{p}\bar{\sigma}\rangle \tag{1.33} \end{align}$$

  One can now derive the time reversal rules for any state.

- You could, quite reasonably, take the following attitude. After all, the $-$ sign in $\boldsymbol{\Theta}^2$ is harmless...no physics changes since the minus sign will not show up in any expectation values. This is, of course, quite true.

- But, wait a sec...the minus sign gives us a crucial theorem regarding half integral spin systems... Let $|\psi\rangle$ be an eigenstate with eigenvalue E of the (time reversal invariant) hamiltonian of the system with half integral spin. Since the hamiltonian is time reversal invariant the state $\boldsymbol{\Theta}|\psi\rangle = |\psi'\rangle$ is also an eigenstate with eigenvalue E. Is $|\psi'\rangle$ a different state from $|\psi\rangle$? If it is then the energy eigenvalue will be degenerate. Let us suppose the contrary that the energy eigenvalue is non-degenerate. Then $|\psi'\rangle = e^{i\alpha}|\psi\rangle$, i. e., the two states are phase related. Now follow the manipulations:

  $$\begin{aligned} \boldsymbol{\Theta}|\psi\rangle &= |\psi'\rangle = e^{i\alpha}|\psi\rangle \\ \boldsymbol{\Theta}^2|\psi\rangle &= \boldsymbol{\Theta}|\psi'\rangle = e^{-i\alpha}\boldsymbol{\Theta}|\psi\rangle = |\psi\rangle \\ \Rightarrow -|\psi\rangle &= |\psi\rangle \end{aligned} \tag{1.34}$$

  which produce an absurd result! What wrong did we do? The mistake: *Assuming* that the state is non-degenerate!

- Kramer's theorem: Every eigenvalue of a half integral spin time reversal invariant hamiltonian is even-fold degenerate. If $|\psi\rangle$ is an eigenstate, $\boldsymbol{\Theta}|\psi\rangle$ is a *different* eigenstate with the same eigenvalue. (☞ An equivalent statement is that one cannot find time reversal invariant eigenstates of a half-integral spin time reversal invariant hamiltonian.)

- Kramer's theorem made a big come back recently...hero in the blockbuster "The dawn of topological insulators"

- Let us summarize: We have reviewed the usual symmetries (translations, rotations) and learned about time reversal symmetry. All of this was done in the hope that it will help us simplify our hamiltonian eqn. (1.1) for atom aggregates. Clearly, this hamiltonian has all these symmetries.

- When we write down a "simpler" hamiltonian, we will try to do so in such a way as to respect as many of the crucial symmetries as possible. We might even deliberately drop some symmetries, or add some! Depends on how desperate we are!

1.2 Scales

- Symmetries in some crude way are "kinematic", i. e., they depend on the "structure" of the states and our hamiltonian.

- There is another thing that we need to do so that we will see a route to writing down a simpler hamiltonian, and even to guess the correct physics of our problem. This is a study of the *energy scales* (or simply "scales") in our problem.

- You will see that uncovering the energy scales of our (or most real) problem(s) is not a trivial task.

- We have five terms in our hamiltonian eqn. (1.1). We need to put down energy scales corresponding to each term. Why is this a useful exercise? This will help us in two ways:

  1. Identify "fast" and "slow" degrees of freedom.
  2. For each set (fast/slow) degrees of freedom we will know which is most important scale – this could allow us to treat other scales in perturbation theory

- Consider the first term in eqn. (1.1) corresponding to the kinetic energy of the ions. What is the energy scale E_I^K corresponding to this? We need a typical momentum scale. We can obtain this from $\hbar/(2M\ell_I^2$ where ℓ_I is the average spacing between the ions! This ℓ_I depends on the volume V of our system...see how the volume of the system sneaked into our consideration! In fact, $\ell_I \sim (\frac{N}{V})^{-1/3} = \rho_I^{-1/3}$ and thus

$$E_I^K = \frac{\hbar^2 \ell_I^{-2}}{2M} = \frac{\hbar^2}{2M}(\rho_I)^{2/3} \tag{1.35}$$

  where ρ_I is the density of ions.

- By the same consideration, we find that the electronic kinetic energy scale E_e^K is given by

$$E_e^K = \frac{\hbar^2 \ell_e^{-2}}{2m} = \frac{\hbar^2}{2m}(\rho_e)^{2/3} \tag{1.36}$$

  where ρ_e is the electronic density. Note that $\ell_e < \ell_I$ since $z > 1$.

- There are three more scales, those that arise from the Coulomb interaction terms.

$$E_{II}^c = \frac{z^2 e^2}{4\pi\epsilon_0 \ell_I}, \qquad E_{Ie}^c = \frac{z e^2}{4\pi\epsilon_0 \ell_{Ie}}, \qquad E_{ee}^c = \frac{e^2}{4\pi\epsilon_0 \ell_e}, \tag{1.37}$$

- Let us simplify life a little bit: if $z \approx 1$, then all the length scales are close to $\ell = \rho^{-1/3}$ where ρ is the density of electrons and ions.

- Thus we get *three* energy scales

$$E^K_I = \frac{\hbar^2}{2M}\rho^{2/3}, \quad E^K_e = \frac{\hbar^2}{2m}\rho^{2/3}, \quad E^C = \frac{e^2}{4\pi\epsilon_0}\rho^{1/3} \tag{1.38}$$

- Let us look at typical numbers. For typical materials, we have

$$E^K_e \approx 1\text{eV}, \quad E^C \lessapprox 1\text{eV}, \quad E^K_I \approx 10^{-4}\text{eV} \tag{1.39}$$

  Electronic kinetic energy is the highest, the coulomb energy is next, and ionic kinetic energy scale is the smallest (because of the large mass of the ions).

- There is actually one more scale in the problem: Temperature T. For example, if T is greater than all the scales given above, then things simplify! We just solve the problem using classical mechanics and we will be perfectly fine. (This is what happens in soft condensed matter). Since we are interested in quantum effects, will consider "low temperatures".

1.3 Approximations and Models

- Now we are in a position to make our first "physically motivated" approximation. First, notice that the energy scale associated with the motion of the ions is four orders of magnitude smaller than that of the electrons. What does really mean? Note that an energy scale in quantum mechanics corresponds to a time scale – the time scale associated with the electrons $\tau_e = \frac{\hbar}{E^K_e}$, and that associated with the ions is $\tau_I = \frac{\hbar}{E^K_I}$!

- Note now that $\tau_I \gg \tau_e$, i. e., ions are far more sluggish compared to the electrons – they move about slowly while the electrons zoom past.

- The electronic coordinates and momenta $(\mathbf{r}_i, \mathbf{p}_i)$ therefore are the *fast* degrees of freedom, while the ionic positions and momenta are the *slow* degrees of freedom.

- This identification slow and fast degrees of freedom suggests an approximation to treat our hamiltonian (1.1)...this was figured out by two very famous physicists.

- Born-Oppenheimer Approximation - we will discuss this at $T = 0$ (can be straight forwardly generalized to $T > 0$) There are two "steps"

  1. Electron motion is fast compared to ion motion. We "freeze" the ions at the some positions $\mathbf{R}_I$, and *solve* the electronic problem. We obtain the electronic ground state and its energy for this frozen positions of the of the ions. Stated in math,

  $$H_e(\{\mathbf{R}_I\})|\Psi^e_G(\{\mathbf{R}_I\})\rangle = E^e_G(\{\mathbf{R}_I\})|\Psi^e_G(\{\mathbf{R}_I\})\rangle \tag{1.40}$$

     (☞ Starting from eqn. (1.1) obtain an expression for $H_e(\{\mathbf{R}_I\})$.) The ground state energy E^e_G *varies* as we move the ions around, i. e, this therefore is like a *potential energy* for the ions!

  2. The Hamiltonian for the ions is therefore

  $$H_I = \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M} + \frac{z^2 e^2}{4\pi\epsilon_0}\sum_{\langle IJ \rangle} \frac{1}{|\mathbf{R}_I - \mathbf{R}_J|} + E^e_G(\{\mathbf{R}_I\}) \tag{1.41}$$

     which can be solved once we know E^e_G as a function of $\{\mathbf{R}_I\}$. (☞ Actually, this is *not* the whole story. The ionic hamiltonian can include "Berry phase" effects that can lead to quite interesting physics.)

3. The ground state energy of H_I is the approximation for the ground state energy of eqn. (1.1), and the ground state wavefunction is

$$|\psi_G^{BO}\rangle = |\psi_G^I\rangle \otimes |\psi_G^e\rangle \tag{1.42}$$

- We might think of celebrating...but alas, the full Born-Oppenheimer program is still too hard...indeed the program as stated above can be taken through only for very small systems like molecules etc!

- What exactly do we mean by too hard? Suppose I ask you what is the crystal structure of Li solid...it will be very hard to find the correct answer purely by the Born-Oppenheimer programme. Instead, one makes reasonable guesses about the possible crystal structure, computes the energies of these reasonable crystal structures using Born-Oppenheimer and picks the one that gives the lowest energy as the ground state. Many *ab initio* electronic structure programmes have been developed to do this.

- Alright, what to do now? Well, how about something drastic? Let take out all the ions out and replace them by a positively charged "jelly" i. e., a uniform density of background positive charge. The density of the jelly is chosen to be precisely such that the positive charge in our volume V cancels the net electronic negative charge – our box is charge neutral. This is called the "jellium model" and is one of the cornerstone models of condensed matter physics.

- The Hilbert space of the jellium model contains only the electronic states, and the hamiltonian is

$$\mathcal{H}_J = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{e^2}{4\pi\epsilon_0} \sum_{\langle ij\rangle} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N} \mathcal{V}_b(\mathbf{r}_i) + E_b \tag{1.43}$$

  the new things are $\mathcal{V}_b(\mathbf{r}_i)$ the potential on the electrons from the uniform background charge, and E_b is the "self electrostatic energy" of the positive jelly.

- Note that the jellium model has all the symmetries of our hamiltonian eqn. (1.1)...we can take solace in this (but not for too long as you will see).

- Can we "solve" the jellium? Alas, no! It is still too hard! But good thing is that some really clever people have worked on this before and have found some very useful tricks to reveal the answer. Learning some of these is part of this course; you will have to wait until you get there.

- Okay, what do we do now? We try to solve the jellium model approximately in some regime.

- What are the scales of the jellium model? There are two E_e^K and E^C. The kinetic energy scale goes as $E_e^K \sim \rho^{2/3}$, while $E^C \sim \rho^{1/3}$. Thus at "large" densities, the kinetic energy dominates over the electrostatic energy. The largeness of density is customarily characterized by a parameter called r_s, defined (modulo constants) as

$$r_s \equiv \frac{E^C}{E_e^K} \approx \frac{\rho^{-1/3}}{a_B} \tag{1.44}$$

  where a_B is the Bohr radius.

- For $r_s \ll 1$, we can drop the electrostatic energy, and we are left with

$$\mathcal{H}_{FE} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \tag{1.45}$$

which is the free electron model which we know and love! (☞ What is(are) the scale(s) of the free electron model?) Note, again, that this model retains all the symmetries of the original hamiltonian eqn. (1.1).

- Free electron model must have been extensively studied in Condensed Matter I, let me just remind you of its successes
    1. Predicts, correctly, the T-linear of the specific heat
    2. Can obtain a formula for conductivity $\sigma = \frac{\rho e^2 \tau}{m}$ (☞ Actually, you need to put more things into the free electron model to get this result. What do you need to put?).
    3. Predicts, correctly, the Widemann-Franz law
    4. ...

- ...and also (two of) its failures...
    - Free electron theory does not have insulators!! All materials will be conductors!!
    - Hall experiments suggest electrons in aluminum are positively charged! But this cannot be obtained from the free electron model.

- Now the first thing is quite disconcerting! There is something crucially wrong...what could it be?

- Clearly we have to do something better! Freezing the ions is unlikely to be wrong since it was based on sound physics arguments regarding the scales of the problems.

- In the jellium model we did something quite drastic - we smeared out the ions. The influence of the ions on the electron motion was only via a *trivial* uniform background potential.

- What happens in aluminium (and other crystalline systems) is that the ions organize themselves in a *periodic fashion*, i. e., they form a lattice. (☞ Make sure that you are thorough with the concept of a lattice. What is a bravais lattice? Give examples of systems that are described by bravais lattice and those that are not, but lattice nevertheless.)

- Recall we had discussed that it is very difficult to show that the ground state of eqn. (1.41) is a crystalline lattice. So we take a pragmatic approach – we *know* from experience (experiment) that the ions form a lattice, we use this as a fact.

- Let us explore what it really means for the ions to organize themselves in a crystalline lattice. First of all ask this: What are the symmetries of the ion hamiltonian eqn. (1.41)? If you reflect a bit, you will see that it has all the symmetries, in particular, translations and rotations.

- We agreed to use the experimental fact that the ground state of H_I corresponds to a crystalline arrangement of atoms. Let the crystal be described by a set of lattice vectors $\{\mathbf{c}_\alpha\}$, then the position of any ion is described by $\mathbf{R}_I = \sum_\alpha n_I^\alpha \mathbf{c}_\alpha$ where n_I^α are (three) integers. If we take (like in the Born-Oppenheimer approximation) that the ions are *fully localized* at these positions, then the ionic ground state is

$$|\Psi^{I}_{G}\rangle = \Pi_{I}|\mathbf{R}_{I}\rangle \tag{1.46}$$

- This all sounds very reasonable. But now if I ask you: Suppose I do a translation of this state, i.e., I apply $\mathcal{T}(\mathbf{a})$ of eqn. (1.8) on this state, what will I get?

$$|\Phi^{I}\rangle \equiv \mathcal{T}(\mathbf{a})|\Psi^{I}_{G}\rangle = \Pi_{I}|\mathbf{R}_{I} + \mathbf{a}\rangle \tag{1.47}$$

  This is still a nice crystalline state of the ions, except that the "origin ion" is now sitting at the position $\mathbf{a}$ of our coordinate system – the relative positions of the ions with the origin atom is unchanged.

- Now since $\mathcal{T}(\mathbf{a})$ is a symmetry of $\mathcal{H}_{I}$, we know $|\Phi\rangle$ is also an eigenstate of $\mathcal{H}_{\mathcal{J}}$ with the same energy. But, what is the relationship between $|\Phi^{I}\rangle$ and $|\Psi^{I}_{G}\rangle$? Well, within our discussion

$$\langle\Phi^{I}|\Psi^{I}_{G}\rangle = 0 \tag{1.48}$$

  i.e., $\mathcal{T}(\mathbf{a})|\Psi^{I}_{G}\rangle$ is *orthogonal* to $|\Psi^{I}_{G}\rangle$!

- Thus the crystalline ground state of the system *breaks* the translational symmetry of the system! This is an example of *broken symmetry* or spontaneous symmetry breaking!

- It is not that the crystalline state does not have any symmetry. Now suppose I choose $\mathbf{a}$ to be a lattice vector, i. e., say $\mathbf{a} = \mathbf{c}_1$ above, then, of course, $\mathcal{T}(\mathbf{a})|\Psi^{I}_{G}\rangle = |\Psi^{I}_{G}\rangle$. In fact, the last result is true for all $\mathbf{a} = \sum_{\alpha} m^{\alpha}\mathbf{c}_{\alpha}$ where m^{α} are integers.

- We thus see that the (translation) symmetry group of the ground state is a now only the set of lattice translations which is a discrete subgroup of our continuous translation group. (☞ Same thing applies to rotations. Once you form a crystal the number of rotations that are symmetries of the ground state wavefunction become smaller).

1.4 Broken Symmetries

- Suppose I have a state $|\Psi\rangle$ and a symmetry operation $\mathcal{U}$, then the state is invariant under $\mathcal{U}$ if

$$\mathcal{U}|\Psi\rangle = e^{i\alpha}|\Psi\rangle \tag{1.49}$$

  for some real α. What this means is that the state obtained the symmetry operation on $|\Psi\rangle$ is the same physical state as $|\Psi\rangle$.

- We have seen how the ions organize themselves in a crystalline form and break the continuous translational symmetry down to lattice translations.

- This idea broken symmetry is a very important one in our taxonomical classification... i.e., in our quest of answering "what all state of electrons is possible".

- Let us understand this better. Once the ions localize at the lattice sites, the ionic potential felt by the electrons no longer has the full continuous translational symmetry, but only the discrete lattice translational symmetry.

- Therefore the symmetries of the electronic system is now discrete lattice translations/rotations, phase symmetry, time reversal symmetry etc.

- Can the electronic state *further* break any of these symmetries?
- The answer is an *emphatic* yes! And the reminder of the course is discovering how and why of this! (☞ Look at the course outline. For each of the “state” mentioned there ask if any symmetry is broken.)