Electronic Hamiltonians - Part III

This will be a much shorter discussion, whose aim is to give you some idea of the difficulties of dealing with strong interactions, and of some of the new physics that appears in such systems. We will use the Hubbard model as our example, and try to understand what happens when U becomes large comparable to t, i.e. interactions are no longer weak and cannot be treated perturbatively. Such systems are called **strongly correlated systems**.

1 The 2-site Hubbard model

Let us consider a system with $N = 2$ ions and $N = 2$ electrons, described by the Hubbard model:

$$\hat{H} = -t \sum_{\sigma} \left(c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma} \right) + U \sum_{i=1}^{2} \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}$$

where $\hat{n}_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ counts how many electrons with spin σ are at site $i = 1, 2$. As discussed, the first term describes hopping of the electrons between (orbitals) associated with the two ions, and the second one is the on-site repulsion when both electrons are occupying the same orbital. We could add more terms, eg a NN repulsion, but we'll assume that that is small enough and can be ignored. For your entertainment, you might want to see what is the effect of such a term, especially if it is not small.

This Hamiltonian describes, for instance, a H_2 molecule if we restrict the electrons to occupy only the $1s$ shells. In that case $t > 0$, which I'll assume to be the case from now on. Again, you might want to wonder what changes if the orbitals involved had different symmetry.

1.1 Free electrons

If $U = 0$ the Hamitonian is quadratic, so we need to find the single-particle states and then occupy them accordingly. For a single electron, we have 4 eigenstates (this is the dimension of our space). The operators associated with them are easily found:

$$c_{\pm,\sigma} = \frac{1}{\sqrt{2}} (c_{1,\sigma} \pm c_{2,\sigma})$$

and their energies are $\epsilon_{\pm} = \mp t$. Note that these are just our tight-binding results for $N = 2$ (in which case the allowed momenta are only $k = 0, \pi$), except for a factor of 2 in the energies. Why is that 2 missing?

For 2 electrons, then, the GS is: $|GS\rangle = c_{+\uparrow}^{\dagger} c_{+\downarrow}^{\dagger} |0\rangle$ and has energy $E_{GS} = -2t$. In the original basis, $|GS\rangle = \frac{1}{2} \left(c_{1\uparrow}^{\dagger} c_{1\downarrow}^{\dagger} + c_{2\uparrow}^{\dagger} c_{2\downarrow}^{\dagger} \right) |0\rangle + \frac{1}{2} \left(c_{1\uparrow}^{\dagger} c_{2\downarrow}^{\dagger} + c_{2\uparrow}^{\dagger} c_{1\downarrow}^{\dagger} \right) |0\rangle$, in other words with probability 1/2 both electrons are at the same site (the first two terms), and with probability 1/2 there is one electron in each orbital. This is reasonable for non-interacting electrons as either one is equally likely to be found at either site, but clearly there is something wrong about this solution if we think about taking the two ions further and further apart. That would decrease the value of t but would not change the wavefunction – although, obviously, if the ions are VERY far apart, there should be zero probability for both electrons to be at the same ion!

This tells us is that in the limit of large distance, U becomes important and our approximation that we can ignore it definitely fails. This is not surprising because U does not depend on the

distance between sites (see its definition, from 2nd quantization), so if this distance becomes large enough and t decreases more and more, we must eventually reach a regime where $t < U$ and then it is wrong to use the $U = 0$ wavefunction as a good approximation.

1.2 HFA

Let us see what HF predicts here. I will assume that in the GS, one electrons is spin-up and one spin-down (the two spin-up or two spin-down eigenstates are very easy to find: $c^\dagger_{1\sigma}c^\dagger_{2\sigma}|0\rangle$ both with $E = 0$. In this case Pauli principle forces the two same-spin electrons to be at different sites and forbids hopping).

We could go through the usual process we discussed, but because we have only 2 electrons let's directly minimize the energy, and avoid the self-consistency loop. Let me take $a^\dagger_\uparrow = \cos\alpha c^\dagger_{1\uparrow} + \sin\alpha c^\dagger_{2\uparrow}$ and $a^\dagger_\downarrow = \cos\beta c^\dagger_{1\downarrow} + \sin\beta c^\dagger_{2\downarrow}$ as the operators associated with the two HF states occupied in the GS, in other words $|HF\rangle = a^\dagger_\uparrow a^\dagger_\downarrow|0\rangle$. The goal is to find the best choice for α, β. For this, we need to calculate $E(\alpha, \beta) = \langle HF|\hat{H}|HF\rangle$ and minimize it (note that the states are already normalized).

After a bit of work, I found:

$$E(\alpha, \beta) = -2t\sin(\alpha + \beta)\cos(\alpha - \beta) + \frac{U}{2}\left[\cos^2(\alpha + \beta) + \cos^2(\alpha - \beta)\right]$$

Let me simplify a bit by introducing the new unknowns $x = \sin(\alpha + \beta), y = \cos(\alpha - \beta)$, in terms of which $E(x, y) = -2txy + \frac{U}{2}[1 - x^2 + y^2]$. We're trying to find its minimum with the constraint $|x| \leq 1, |y| \leq 1$. Just taking derivatives doesn't work because this function does not have a local minimum inside this region of interest (or maybe I made some mistakes, let me know). So the way I went about it is to rewrite:

$$E(x, y) = \frac{U}{2}\left[y - \frac{2tx}{U}\right]^2 + \frac{U}{2}\left[1 - x^2(1 + \frac{4t^2}{U^2})\right]$$

To minimize this, ideally we would choose $x = \pm 1$ (to make the second term as negative as possible) and $y = 2tx/U$ (to make the first square as small as possible). However, we can only have both simultaneously if $U \geq 2t$, because we must have $|y| \leq 1$,

So: for $U \geq 2t$, the solution is $x = \pm 1, y = \pm 2t/U \rightarrow E_{HF} = -\frac{2t^2}{U}$.

For $U \leq 2t$, we cannot have both simultaneously. The best solution here is to keep $x = \pm 1$ and now take $y = \pm 1$, so that we minimize the quantity we square in the first term. With this, I find $E_{HF} = -2t + \frac{U}{2}$. Some Maple work plotting this function confirmed my guess, so I think this is the true minimum – but let me know if you disagree.

In any event, this suggests that E_{HF} looks somewhat like the sketch below. For small U/t the wavefunction is precisely the one we had for free electrons, in other words this is the 2-site equivalent of a "metal", where every electron is equally shared between all sites. In the limit $U/t \rightarrow \infty$, on the other hand, we have $\alpha + \beta = \frac{\pi}{2}, \alpha - \beta \rightarrow \pm\frac{\pi}{2}$ showing that the up-spin is entirely at one site and the down-spin at the other site – which agrees with our intuition that in this limit, we should have two neutral atoms. But it also suggests that now their electrons prefer to have opposite spins, because that leads to a lower energy than they having the same spin.

The question is: can we believe this large-U HF prediction? Luckily, this problem is so simple that we can solve it exactly to see what is the true ground-state.

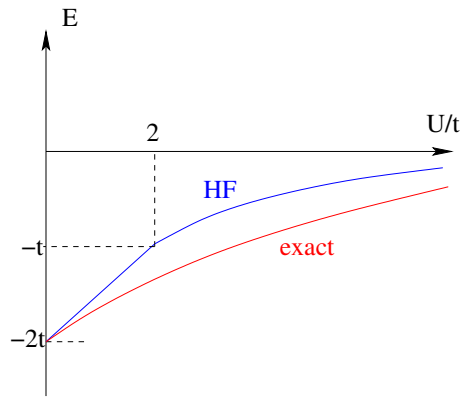

Figure 1: Sketch of HF vs. exact ground-state energy.

1.3 Exact solution

The Hilbert space is small enough that we can easily find all the eigenstates. I'll only write the solution for the subspace that contains the GS and I'll let you verify that all other eigenstates have higher energies than this. For reasons of symmetry (see more discussion along these lines in the first homework, for the 3-site Hubbard model), we expect the GS to be symmetric and with a spin-up and a spin-down; the most general guess is:

$$|\Psi\rangle = \alpha \left(c^\dagger_{1\uparrow} c^\dagger_{1\downarrow} + c^\dagger_{2\uparrow} c^\dagger_{2\downarrow} \right) |0\rangle + \beta \left(c^\dagger_{1\uparrow} c^\dagger_{2\downarrow} + c^\dagger_{2\uparrow} c^\dagger_{1\downarrow} \right) |0\rangle$$

Asking that $\hat{H}|\Psi\rangle = E|\Psi\rangle$ leads to the coupled equations $(E-U)\alpha + 2t\beta = 0; 2t\alpha + E\beta = 0$. This has two non-trivial solutions; the one with the lower energy is the ground-state:

$$E_{GS} = \frac{1}{2}[U - \sqrt{U^2 + 16t^2}]$$

and its coefficients are such that $\alpha/\beta = -E_{GS}/2t$.

In the limit $U/t \to 0$, $E_{GS} \approx -2t + \frac{U}{2} - \frac{U^2}{16t^2} + \ldots$, i.e. it is below the HF energy (as it has to be!) but not by a lot. We also see that $\alpha/\beta \to 1$, which also agrees with the HF solution.

In the limit $U/t \to \infty$, $E_{GS} \approx -\frac{4t^2}{U} + \ldots$, so it is twice smaller than HF. Here, $\alpha/\beta \to -2t/U \to 0$, showing that indeed the probability to have both electrons at the same site vanishes like $\sim t^2/U^2$. We also see that the true GS is a singlet between the two electrons, not the HF prediction that one electron (say, spin-up) is on the left ion and the other one on the right one, or viceversa. The singlet makes better sense because there is nothing to distinguish the two ions, thus no reason why they would have different permanent magnetic moments associated with their electrons. BUT: the singlet is not a Slater determinant, so the best HF can do is to mimic the tendency for AFM order (singlet) by freezing electrons with AFM spins on the two sites (this also explains the higher HF energy prediction).

So we see that HF gets the trends right: it predicts that the system is "metallic" at small U/t (i.e., any electron is equally likely to be found at any site and the energy is dominated by the kinetic energy contribution), but becomes "insulating" at large U/t, where the wavefunction has one electron per site. Even though the electrons are localized at one per site (which is now

favourable in order to avoid the large cost U of having two electrons per site), there is the spin degree of freedom associated with each electron, and they order in a singlet, i.e. as if there is AFM coupling between the electrons (more on this below). HF doesn't get this fully right, but at least it mimics the AFM tendency. HF also predicts a transition between the two regimes, there is a discontinuity in the (slope) of E_{HF} at $U/t = 2$ – again, that is not correct, but it's the best HF can do to mimic the two regimes. So one always has to be careful with which parts of HF predictions to believe, and which not.

Is it making sense that the spins of the electrons would prefer AFM order in the insulating phase, i.e. when there is one electron per ion? The answer is yes. As we saw, for FM (parallel) spins, Pauli principle forbids any electron from hopping to its neighbour and the energy is zero $E_{\uparrow\uparrow} = E_{\downarrow\downarrow} = 0$. On the other hand, if the spins are antiparallel, then each electron can make short "visits" to the other site. The "visit" (officially known as *virtual hopping*) is short so as to avoid paying the large cost U – indeed, the coefficient α becomes very small – but the energy is lowered a bit because the electron moves so the kinetic energy contributes a bit. Note: you can also make a triplet state from an spin up and a spin-down – you should check that its energy is also zero, like you should have expected (why?).

This tells us that in the large U/t limit, if we're interested only in the low-energy properties of the system, we can replace the 2-site Hubbard Hamiltonian with a simpler Hamiltonian describing the coupling between the spins $\hat{\vec{s}}_1, \hat{\vec{s}}_2$ of the electrons localized at the two sites:

$$\hat{H}_J = J\left(\hat{\vec{s}}_1 \cdot \hat{\vec{s}}_2 - \frac{1}{4}\right)$$

where $J = 4t^2/U$. This is know as the **Heisenberg Hamiltonian**. You should check that indeed, when applied to a singlet this Hamiltonian predicts a GS energy of $-J$, whereas for a triplet state it predicts 0 – in other words, it mimics what the Hubbard model predicts in the strongly-correlated limit. But only at low energies! The Hubbard model also has eigenstates with high energy $\sim U$ which are not described by this simpler Hamiltonian.

One important aspect to emphasize is how large this J is. Of course the exact magnitude will depend on various details of the material, but it is typically in the $0.1-1$eV range. This is important because you might think that of course we should have expected AFM order between the spins of the electrons, when the electrons are localized – because there is a magnetic moment associated with each spin, and there is dipole-dipole interaction between magnetic moments which will favour some kind of magnetic order. However, the strength of the dipole-dipole interactions is many (~ 4) orders of magnitude smaller than this J we got because of Coulomb interactions combined with the Pauli principle! In other words, dipole-dipole interactions can and are usually ignored in most materials without any problem (of course, every rule has exceptions, and there are materials where, for various reasons, the dipole-dipole interactions are the only type of magnetic coupling and dominate the magnetic properties, although this is restricted to very low temperatures, of the order $1K$. At higher temperatures the thermal energy k_BT is large enough to scramble between all magnetic orientations since the energy difference between them is so small). This is why insulators that show magnetic order up to high temperatures (hundreds of K), do so because of this interplay between Coulomb repulsion and Pauli principle! We will come back to this towards the end of the term, when I hope we'll have time to discuss magnetic insulators and their properties in more detail.

The last question to address now, is how relevant all this is for the macroscopic systems, with $N \sim 10^{23}$, not $N = 2$. It turns out that quite a bit carries over. In a 3D lattice, if we have one electron per site (this is known as **half-filing**), for weak U/t the system is found to be metallic,

i.e. one can add or remove an electron with zero energy cost (the Fermi energy is inside a partially filled band). For large U/t, on the other hand, the system is insulating (the Fermi energy is inside a gap) but acquires AFM order. In fact, one can show that the mapping to an AFM Heisenberg model with $J = 4t^2/U$ remains true in this limit – you may get this as a homework problem. So there is a **metal-insulator transition** (MIT) as the repulsion U/t increases, and this is due to correlations! This is the **Mott transition** that I mentioned before, and the insulator is called a **Mott insulator**.

What is meant by "small" and "large" U/t depends on various details (also, so far we only have numerical solutions or approximations for dealing with 3D systems, so there is some uncertainty because of not being able to solve this exactly. But there is broad agreement between multiple approaches that there is a MIT as U increases, in 3D). The only exact solution we have is for a 1D Hubbard chain, based on the so-called **Bethe ansatz** (in fact, I believe there is some controversy whether the Bethe ansatz gives all the eigenstates or it misses some – but I think there is agreement that it predicts the correct GS. This is not a field I am particularly acquainted with, so if any of you knows more please let me know). In any event, the Bethe ansatz solution predicts that the 1D Hubbard model, at half-filling, becomes an insulator for any $U/t > 0$, and it is only a metal at $U = 0$ (although, as we'll see later, even then it will attempt to become insulating by other means: 1D systems just don't like to be metallic).

The 2D is the less understood case. Here we don't have an exact solution, and good numerics/approximations are harder to find because of the need to deal with the quantum fluctuations, which are much stronger in lower dimensions, and thus more of a serious problem than in 3D. So far as I know, the current consensus is that the 2D Hubbard model on the square lattice also becomes insulating for any $U \neq 0$, but this is still an area of research. Other lattices, eg the hexagonal one, may be even more interesting because of so-called frustration (we'll discuss what this means towards the end of the course). If any of these topics are in your area of expertise, let me know what is the current understanding so that I can update these notes accordingly.