Title: Date:

3. The electronic structure problem

* You know the Hubbard and t-J models
* You can perform a mean-field calculation
* You can say what DFT is and you can name and describe a few code-codes

Arguably the most important many-body quantum problem is the one of interacting electrons. On one hand, it determines most properties of matter. On the other hand we typically deal with $\mathcal{O}(10^{23})$ particles. Knowing that the Hilbert-space grows exponentially with the number of particles turns the solution of the electronic structure problem into a daunting task. In this chapter we learn several approximate methods to deal with this problem. This means, we might be able to deal with systems not accessible to exact methods like quantum Monte Carlo or exact diagonalization. This comes at the price of systematic errors and biases however. For problems where the kinetic energy dominates over other scales, we can gain a lot of useful insights!

3.1 Statement of the problem

For many atoms, molecules, and solids, the ionic core is much heavier than the electrons. This means we can solve for the solution of the electronic problem

while keeping the coordinates of the ionic cores fixed. Using this Born-Oppenheimer approximation, the Hamiltonian reads

$$H = \sum_{i=1}^{N} \left[-\frac{\hbar \nabla_i^2}{2m} - \underbrace{\sum_{j=1}^{M} \frac{Z_j e^2}{|\vec{R}_j - \vec{r}_i|}}_{V(\vec{r}_i)} \right] + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|},$$

where $\vec{R}_j$ are the (fixed) ionic positions and Z_j is the charge of ion j. The Car-Parinello method that we discuss later calculates forces on the $\vec{R}_j$'s after having solved the electronic problem.

Clearly, we will want to write the above Hamiltonian in second quantization. For that, we use single-particle wave-functions $f_i(\vec{r})$ to write

$$t_{ij} = \int d\vec{r}\, f_i^*(\vec{r}) \left[-\frac{\hbar \nabla_i^2}{2m} + V(\vec{r}) \right] f_j(\vec{r}) \quad \text{and}$$

$$V_{ijkl} = \int d\vec{r}\, d\vec{s}\, f_i^*(\vec{r}) f_k^*(\vec{s}) \frac{e^2}{|\vec{r} - \vec{s}|} f_j(\vec{r}) f_l(\vec{s})$$

Using these coefficients we find

$$H = \sum_{ij,\sigma} t_{ij}\, c_{i\sigma}^+ c_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl}\, c_{i\sigma}^+ c_{k\sigma'}^+ c_{j\sigma'} c_{l\sigma}.$$

We obviously adapt the choice of f_i to the problem at hand. For a free-space problem of many electrons we might choose plane waves $e^{i\vec{k}\vec{r}}$. For electronic

Title: Date:

Problems of atoms and molecules we would take the solutions of the Hydrogen atom, or at least spherical harmonics of the relative coordinates, etc.

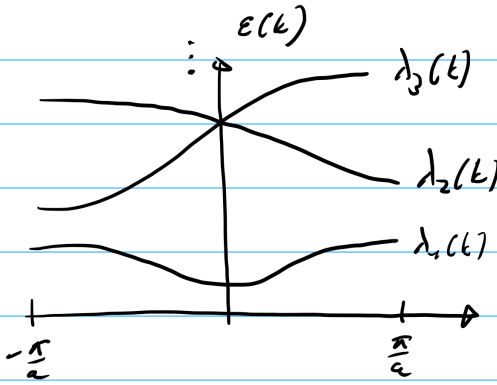
9.2. Electrons in solids

For electrons in solids we know the we should take Bloch waves

$$\psi_k^\alpha(\vec{r}) = e^{i\vec{k}\vec{r}} \cdot u_k^\alpha(\vec{r}) \qquad \text{with} \quad \vec{k} \in [-\pi/a, \pi/a]^d$$

and $u(\vec{r} + n a \hat{e}_x + m a \hat{e}_y + l a \hat{e}_z) = u(\vec{r})$ with $n,m,l \in \mathbb{N}$.
(we chose a simple cubic lattice here) We also know that the free spectrum is given by bands

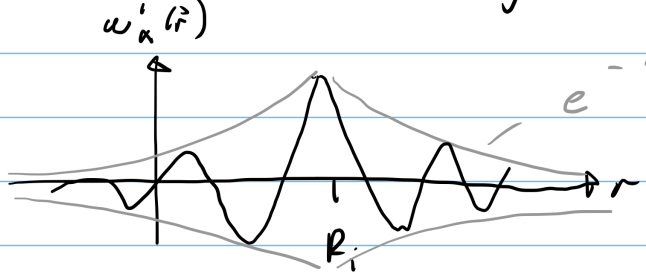
$$H \psi_k^\alpha(\vec{r}) = \lambda_\alpha(\vec{k}) \psi(\vec{r})$$



If we only want to describe the physics in one band, we use the Wannier states of the respective band

$$w_\alpha^i(\vec{r}) = \int dk \; u_k^\alpha(\vec{r}) \, e^{i\vec{k}(\vec{r}-\vec{R}_i)}$$

location of Wannier center



Title: Date:

In this setup, the interacting problem on a single band is typically well-approximated by

$$H = -t \sum_{\langle ij \rangle, \sigma} c_{i\sigma}^{\dagger} c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

In other words: electrons only hop to neighboring sites and the interaction is only active on the same site. This is of course only a good approximation if the long-range Coulomb interaction is screened.

Before we attempt an approximate solution of the above Hubbard model, we discuss two limiting models: For very strong interactions $U \gg t$, sites will never be doubly occupied. If we are at half filling, i.e. one particle per site, we can reduce the Hubbard model to the Heisenberg model

$$H = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \vec{S}_j + \text{const}$$

where

$$J_{ij} = \frac{4 t_{ij}^2}{U}$$

[go through perturbation theory in $\frac{t}{U}$ to derive this result ⊥

If we remove a finite density of particles from half-filling, these additional holes can move freely without introducing an energy penalty U. The corresponding Hamiltonian is known as the t-J-model

$$H = \sum_{\langle i,j\rangle,\sigma} -t \Big[\overbrace{(1-n_{i,-\sigma})\, c_{i\sigma}^{\dagger} c_{j\sigma}}^{P_{i\sigma}} \overbrace{(1-n_{j,-\sigma})}^{P_{j\sigma}} + \text{H.c.} \Big] + \sum_{\langle ij\rangle} J_{ij} \Big[\vec{S}_i \vec{S}_j - \tfrac{1}{2} n_i n_j \Big]$$

where $n_i = n_{i\uparrow} + n_{i\downarrow}$. Note that $P_{i\sigma}$ and $P_{j\sigma}$ make sure that we never hold two particles on one site, greatly reducing the Hilbert space size!

3.2.1 Hartree-Fock

The first approximative method we learn is the Hartree-Fock idea. The assumption is stated in simple terms: We assume the many-body wave function to be a Slater determinant

$$\psi(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2, \ldots, \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N}} \begin{vmatrix} \phi_1(r_1\sigma_1) & \cdots & \phi_1(r_N\sigma_N) \\ \vdots & \ddots & \vdots \\ \phi_N(r_1\sigma_1) & \cdots & \phi_N(r_N\sigma_2) \end{vmatrix}.$$

For a free-electron system, this is of course the exact ground state if we use for $\phi_1, \ldots, \phi_N$ the N lowest single particle states. However, for the case of interacting systems the task is to find suitable wave functions $\phi_1 \ldots \phi_N$ such that the ground state energy is minimized. There are two routes to do so:

Route 1: We write $\psi = \prod_{\mu\sigma}^{N} c_{\mu\sigma}^{\dagger} |0\rangle$ and need to find the N best orbitals.

Title: Date:

For that we write

$$c^{+}_{\mu\sigma} = \sum_{i=1}^{L} d_{\mu i}\, c^{+}_{i\sigma}$$

(Here are the $L \times N$ coefficients we need to optimize)

we write

$$1 = \langle \phi_\mu | \phi_\mu \rangle = \sum_{ij} d^{*}_{\mu i} d_{\mu j} S_{ij}$$

from which we find

$$\tilde{E} = \langle \psi | H | \psi \rangle - \sum_{\mu} \varepsilon_\mu \sum_{ij} d^{*}_{\mu i} d_{\mu j} S_{ij}$$

and now minimize $\tilde{E}$ over $d_{\mu i}$.

Route 2: There is a second, somewhat more transparent approach. Above we had a large set of free parameters $d_{\mu i}$.

We know a simple way, however, to generate orthonormal wave functions used for a Slater-determinant with only **a few simple parameters**: The ground state of a **quadratic Hamiltonian**. In other words, a few parameters in a trial Hamiltonian determine a full set of wave-functions!

Example let us say we want to find a good wave function for the **negative U Hubbard model**

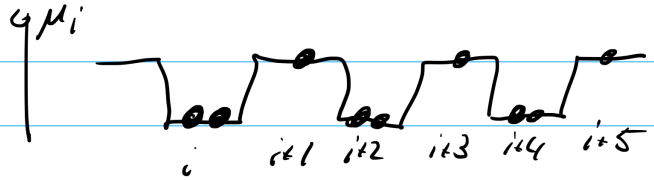
$$H = \sum_{ij\sigma} -t_{ij}\, c^{+}_{i\sigma} c_{j\sigma} + \text{h.c.} - \mu \sum_{i\sigma} c^{+}_{i\sigma} c_{i\sigma} - |U| \sum_i n_{i\uparrow} n_{i\downarrow}$$

Title: Date:

Our trial (or mean-field) Hamiltonian looks like

$$H_{MF} = \sum_{ij\sigma} -t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + h.c. - \sum_{i\sigma} \mu_i c_{i\sigma}^{\dagger} c_{i\sigma} - \sum_i \Delta_i c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} + h.c.$$

The μ_i control the charge order in the wave function as e.g. a stagger $\mu_i = (-1)^{n_i + m_i}$ would periodically favor or punish sites



The second parameter Δ_i controls the appearance of superconductivity.

What we now need to do, is to minimize the energy

$$\langle H \rangle_{MF} = \langle H_{MF} \rangle_{MF} - \langle \sum_{i\sigma} (\mu - \mu_i) c_{i\sigma}^{\dagger} c_{i\sigma} + \sum_i \Delta_i c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} + h.c. - |U| \sum_i n_{i\uparrow} n_{i\downarrow} \rangle_{MF}$$

where $\langle \cdot \rangle_{MF}$ is the expectation value with respect to the ground state Slater determinant of H_{MF}. To minimize the above expression we demand

$$\frac{\partial \langle H \rangle_{MF}}{\partial \Delta_j} = \frac{\partial \langle H \rangle_{MF}}{\partial \mu_j} = 0 \qquad \forall_j$$

Let us do this:

Title: Date:

$$\frac{\partial}{\partial \Delta_j}\langle H\rangle_{MF} = \frac{\partial}{\partial \Delta_j}\langle H_{MF}\rangle_{MF} - \sum_{i\sigma}(\mu-\mu_i)\frac{\partial}{\partial \Delta_j}\langle c_{i\sigma}^{\dagger}c_{i\sigma}\rangle_{MF}$$

$\rightarrow \langle \partial_{\Delta_j} H_{MF}\rangle_{MF}$

$$+\langle c_{i\uparrow}^{\dagger}c_{i\downarrow}^{\dagger}\rangle_{MF} + \text{h.c.} + \sum_i \Delta_i \frac{\partial}{\partial \Delta_j}\langle c_{i\uparrow}^{\dagger}c_{i\downarrow}^{\dagger}\rangle_{MF}$$

$$\sum_i \Delta_i^{*}\frac{\partial}{\partial \Delta_j}\langle c_{i\sigma}c_{i\bar{\sigma}}\rangle_{MF}$$

$$-|u|\sum_i \frac{\partial}{\partial \Delta_i}\Big[\langle c_{i\sigma}^{\dagger}c_{i\bar{\sigma}}^{\dagger}\rangle_{MF}\langle c_{i\sigma}c_{i\bar{\sigma}}\rangle_{MF} + \langle c_{i\sigma}^{\dagger}c_{i\bar{\sigma}}\rangle_{MF}\langle c_{i\bar{\sigma}}^{\dagger}c_{i\sigma}\rangle_{MF}\Big]$$

The Hellmann - Feynman theorem

$$H(\lambda)|\psi(\lambda)\rangle = \varepsilon_\lambda |\psi(\lambda)\rangle \Rightarrow \frac{\partial}{\partial\lambda}\langle\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle =$$

$$= \langle\partial_\lambda\psi(\lambda)|H(\lambda)|\psi(\lambda)\rangle + \langle\psi(\lambda)|\partial_\lambda H(\lambda)|\psi(\lambda)\rangle +$$

$$\langle\psi(\lambda)|H(\lambda)|\partial_\lambda\psi(\lambda)\rangle = \varepsilon_\lambda\big(\langle\partial_\lambda\psi|\psi\rangle + \langle\psi|\partial_\lambda\psi\rangle\big)$$

$$+\langle\psi|\partial_\lambda H|\psi\rangle = \varepsilon_\lambda \underbrace{\partial_\lambda\langle\psi|\psi\rangle}_{1} + \langle\partial_\lambda H\rangle = \langle\partial_\lambda H\rangle$$

$$\Rightarrow \partial_{\Delta_j}\langle H_{MF}\rangle_{MF} = \langle\partial_{\Delta_j}H_{MF}\rangle_{MF} = -\langle c_{i\uparrow}c_{i\downarrow}^{\dagger}\rangle_{MF} + \text{h.c.}$$

$$\Rightarrow \frac{\partial}{\partial\Delta_j}\langle H\rangle_{MF} = \sum_i\Big[-(\mu-\mu_i) - |u|\langle c_{i\sigma}^{\dagger}c_{i\sigma}\rangle_{MF}\Big]\frac{\partial}{\partial\Delta_j}\langle c_{i\downarrow}^{\dagger}c_{i\downarrow}\rangle_{MF} + (\uparrow\to\downarrow)$$

$$+\sum_i\Big[\Delta_i - |u|\langle c_{i\sigma}c_{i\bar{\sigma}}\rangle_{MF}\Big]\frac{\partial}{\partial\Delta_j}\langle c_{i\sigma}^{\dagger}c_{i\bar{\sigma}}^{\dagger}\rangle_{MF} + \text{h.c.}$$

for $\frac{\partial}{\partial \mu_j}$ we get the same terms with $\frac{\partial}{\partial \Delta_j}\langle \dots \rangle$ replaced by $\frac{\partial}{\partial \mu_j}\langle \dots \rangle$. We can now make the quite general assumption that

$$\begin{pmatrix} \frac{\partial}{\partial \Delta_j}\langle c_{i\uparrow}^{+} c_{i\downarrow}^{+} \rangle_{MF} & \frac{\partial}{\partial \Delta_j}\langle c_{i\uparrow}^{+} c_{i\uparrow} \rangle_{MF} \\ \frac{\partial}{\partial \mu_j}\langle c_{i\uparrow}^{+} c_{i\downarrow}^{+} \rangle_{MF} & \frac{\partial}{\partial \mu_j}\langle c_{i\uparrow} c_{i\uparrow} \rangle_{MF} \end{pmatrix}$$

is non-singular. Then we need to set all pre-factors the zero to find a minimum of the variational energy.

$$\Delta_i = |U| \langle c_{i\uparrow} c_{i\downarrow} \rangle_{MF}$$

$$\mu_i = \mu + |U| \sum_{\sigma} \langle c_{i\sigma}^{+} c_{i\sigma} \rangle_{MF}$$

Self-consistency equations for μ_i, Δ_i

We see that we deal with a problem where H_{MF} depends on Δ_i, μ_i which in turn makes $\langle \dots \rangle_{MF}$ depend on Δ_i, μ_i $\Rightarrow$ we deal with a non-linear problem. This happens quite often: Approximate methods render the linear quantum mechanics into a non-linear problem.

We have two routes again to fulfill the above equations: the solver exactly for the eigenstates of H_{MF}. Then we can try to solve the above equations exactly. Or we iterate:

Title: Date:

(i) Assume initial values Δ_i, μ_i

(ii) Solve H_{MF} numerically

(iii) Calculate $\langle c_{i\uparrow}^{\dagger} c_{i\downarrow}^{\dagger} \rangle_{MF}$ and $\langle c_{i\sigma}^{\dagger} c_{i\sigma} \rangle_{MF}$

(iv) Use the self-consistency equations to obtain new Δ_i, μ_i

(v) Repeat until you reach convergence.

Known problems

Slow convergence / oscillatory behavior of μ_i, Δ_i

Level 1 solution: $\Delta_i^{n+1} = (1-\alpha)\Delta_i^{n} + \alpha \Delta_i^{n-1}$

$\mu_i^{n+1} = (1-\alpha)\mu_i^{n} + \alpha \mu_i^{n-1}$

with $\alpha \in [0,1[$

Level 2 solution: Broyden algorithm: Conjugate gradient method to determine $\{\Delta_i^{n+1}, \mu_i^{n+1}\}$