

PY4T01 Condensed Matter Theory: Lecture 16

Mean field approximation

Can we solve the many-particle problem?

$$H_U = \epsilon_0 \sum_{\mu\sigma} \hat{n}_{\mu\sigma} + \gamma \sum_{\sigma} (c_{1\sigma}^\dagger c_{2\sigma} + c_{2\sigma}^\dagger c_{1\sigma}) + U \sum_{\mu} \hat{n}_{\mu\uparrow} \hat{n}_{\mu\downarrow}$$

Let us re-write the Hubbard term

$$\begin{aligned} U \sum_{\mu} \hat{n}_{\mu\uparrow} \hat{n}_{\mu\downarrow} &= U \sum_{\mu} [n_{\mu\uparrow} - (n_{\mu\uparrow} - \hat{n}_{\mu\uparrow})] [n_{\mu\downarrow} - (n_{\mu\downarrow} - \hat{n}_{\mu\downarrow})] = \\ &= U \sum_{\mu} [n_{\mu\uparrow} - \delta\hat{n}_{\mu\uparrow}] [n_{\mu\downarrow} - \delta\hat{n}_{\mu\downarrow}] \end{aligned}$$

with $n_{\mu\sigma} = \langle \hat{n}_{\mu\sigma} \rangle$ and we have introduced the *fluctuation* operator $\delta\hat{n}_{\nu\sigma}$

By expanding we obtain

$$U \sum_{\mu} \hat{n}_{\mu\uparrow} \hat{n}_{\mu\downarrow} = U \sum_{\mu} [n_{\mu\uparrow} n_{\mu\downarrow} - n_{\mu\uparrow} \delta\hat{n}_{\mu\downarrow} - n_{\mu\downarrow} \delta\hat{n}_{\mu\uparrow} + \delta\hat{n}_{\mu\downarrow} \delta\hat{n}_{\mu\uparrow}]$$

The **mean field approximation** consists in neglecting the fluctuation-fluctuation term

$$U \sum_{\mu} \hat{n}_{\mu\uparrow} \hat{n}_{\mu\downarrow} \approx U \sum_{\mu} [n_{\mu\uparrow} n_{\mu\downarrow} - n_{\mu\uparrow} \delta \hat{n}_{\mu\downarrow} - n_{\mu\downarrow} \delta \hat{n}_{\mu\uparrow}] =$$

$$U \sum_{\mu} [n_{\mu\uparrow} \hat{n}_{\mu\downarrow} + n_{\mu\downarrow} \hat{n}_{\mu\uparrow} - n_{\mu\uparrow} n_{\mu\downarrow}]$$

This is now a single-particle Hamiltonian!

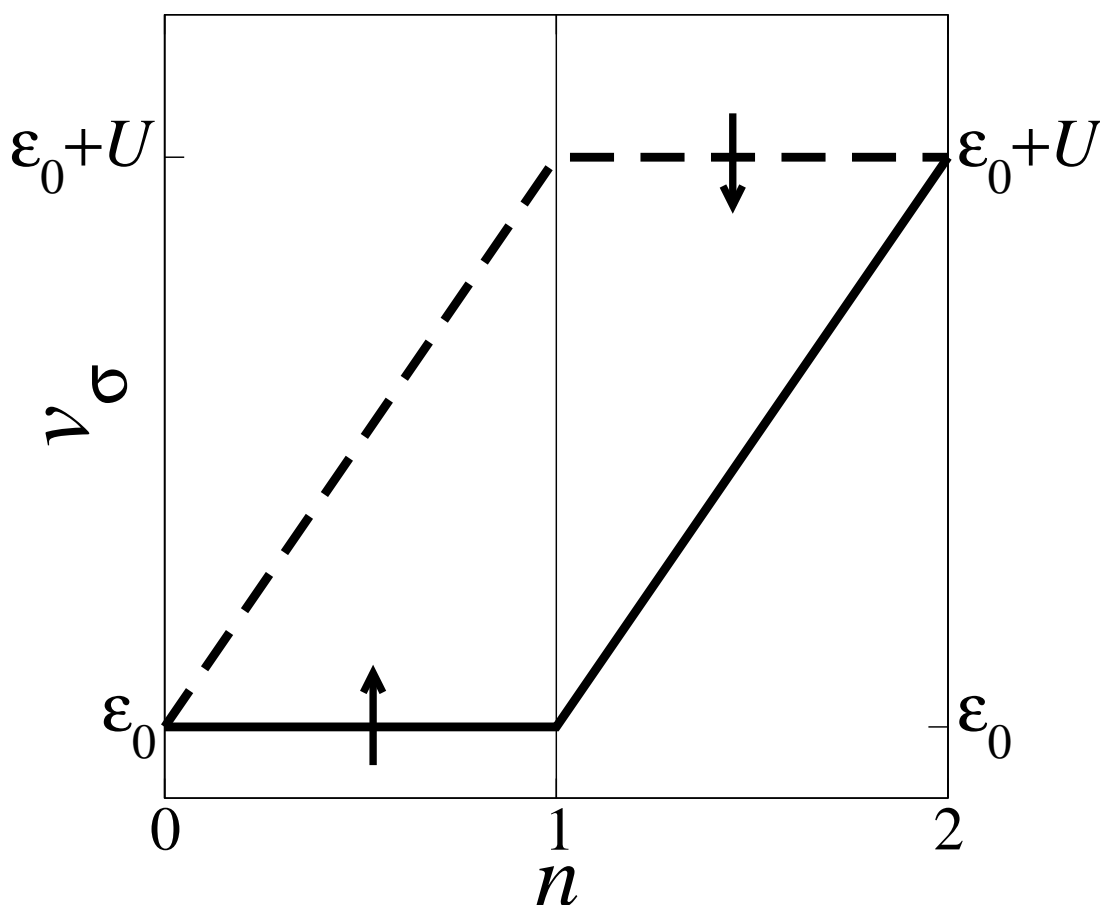
$$\begin{aligned} H_U = & \sum_{\mu} [\hat{n}_{\mu\uparrow} (\epsilon_0 + U n_{\mu\downarrow}) + \hat{n}_{\mu\downarrow} (\epsilon_0 + U n_{\mu\uparrow})] + \\ & + \gamma \sum_{\sigma} (c_{1\sigma}^{\dagger} c_{2\sigma} + c_{2\sigma}^{\dagger} c_{1\sigma}) + \\ & - U \sum_{\mu} n_{\mu\uparrow} n_{\mu\downarrow} \end{aligned}$$

where the on-site energy depends on the spin-occupation $n_{\mu\sigma}$

In general one needs a self-consistent solution, i.e. we have to determine $n_{\mu\sigma}$. For the case of H_2 this is however simple.

How does the new on-site (mean field) term work? Consider the case of one atom only.

$$H_0 = \hat{n}_\uparrow(\epsilon_0 + Un_\downarrow) + \hat{n}_\downarrow(\epsilon_0 + Un_\uparrow) = \hat{n}_\uparrow v_\downarrow + \hat{n}_\downarrow v_\uparrow$$



The potential for spin \uparrow depends on the population of spin \downarrow and viceversa.

Let us revise the **N=2** case.

Since now there is no electron-electron operator (no operator in $c^\dagger c^\dagger c c$) we can simply use

$$|\psi\rangle = \psi_1 |\uparrow, 0\rangle + \psi_2 |0, \uparrow\rangle$$

or

$$|\psi\rangle = \psi_1 |\downarrow, 0\rangle + \psi_2 |0, \downarrow\rangle$$

Take for instance spin \uparrow . The Hamiltonian matrix then is

$$\begin{pmatrix} \epsilon_0 + U n_{1\downarrow} & \gamma \\ \gamma & \epsilon_0 + U n_{2\downarrow} \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = E \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}$$

This is formally the Hamiltonian equation for the heteronuclear molecule. However because H_2 is homonuclear then one has $n_{1\sigma} = n_{2\sigma} = 1/2 n_\sigma$ (this is because of inversion symmetry). The the solution is:

$$E_{\text{bond}}^\uparrow = \epsilon_0 + \frac{U}{2} n_\downarrow + \gamma, \quad |\psi_{\text{bond}}\rangle = \frac{1}{\sqrt{2}} [|\uparrow, 0\rangle + |0, \uparrow\rangle]$$

$$E_{\text{anti}}^\uparrow = \epsilon_0 + \frac{U}{2} n_\downarrow - \gamma, \quad |\psi_{\text{anti}}\rangle = \frac{1}{\sqrt{2}} [|\uparrow, 0\rangle - |0, \uparrow\rangle]$$

Now repeat the same for \downarrow

$$E_{\text{bond}}^{\downarrow} = \epsilon_0 + \frac{U}{2}n_{\uparrow} + \gamma, \quad |\psi_{\text{bond}}\rangle = \frac{1}{\sqrt{2}} [| \downarrow, 0\rangle + |0, \downarrow\rangle]$$

$$E_{\text{anti}}^{\downarrow} = \epsilon_0 + \frac{U}{2}n_{\uparrow} - \gamma, \quad |\psi_{\text{anti}}\rangle = \frac{1}{\sqrt{2}} [| \downarrow, 0\rangle - |0, \downarrow\rangle]$$

Finally calculate the ground state energy for two electrons (\uparrow and \downarrow). Note that $n^{\uparrow} = n^{\downarrow} = 1$, then

$$E_{\text{bond}}^{\uparrow} = E_{\text{bond}}^{\downarrow} = \epsilon_0 + \frac{U}{2} + \gamma$$

$$E_{\text{anti}}^{\uparrow} = E_{\text{anti}}^{\downarrow} = \epsilon_0 + \frac{U}{2} - \gamma$$

The total energy finally is

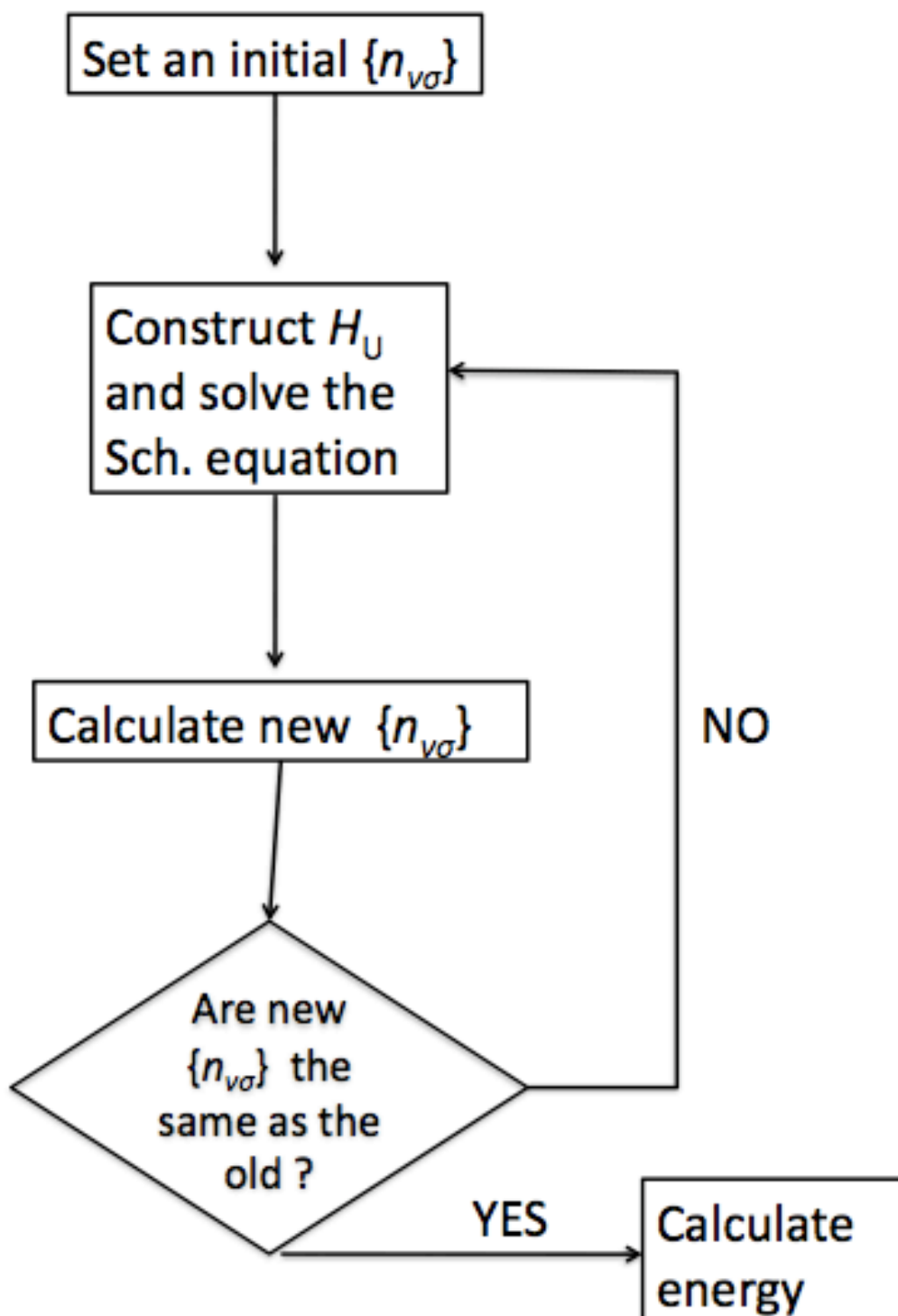
$$E_{\text{total}} = E_{\text{bond}}^{\uparrow} + E_{\text{bond}}^{\downarrow} - U \sum_{\mu} n_{\mu\uparrow} n_{\mu\downarrow}$$

$$E_{\text{total}} = 2(\epsilon_0 + \gamma) + U/2$$

to compare with that of the fully interacting case

$$E_{\text{total}} = 2\epsilon_0 + \frac{U}{2} - \frac{\sqrt{U^2 + 16\gamma^2}}{2} \approx 2(\epsilon_0 - |\gamma|) + U/2 - \frac{|\gamma|U^2}{16\gamma^2}$$

If $n_{\mu\sigma}$ are not known *a priori* then the calculation needs to be self-consistent:



Functional theory

Is there a better and more precise way of finding the ground state energy? Yes, one can define the problem via a *variational principle*

$$E_{\text{GS}} = \min_{|\Psi\rangle} \langle \Psi | H_{\text{U}} | \Psi \rangle, \quad \langle \Psi | \sum_{\mu\sigma} \hat{n}_{\mu\sigma} | \Psi \rangle = N$$

One has to search for the $|\Psi\rangle$ that minimizes the functional \rightarrow still an impossible task (the Hilbert space for $|\Psi\rangle$ is enormous).

What if the many-particle wave-function is itself a functional of some simpler quantity? For instance

$$|\Psi\rangle = |\Psi[\{n_{\mu\sigma}\}]\rangle$$

then

$$E_{\text{GS}} = \min_{\{n_{\mu\sigma}\}} \langle \Psi[\{n_{\mu\sigma}\}] | H_{\text{U}} | \Psi[\{n_{\mu\sigma}\}] \rangle$$

One now has to find the set of occupation numbers $\{n_{\mu\sigma}\}$ which minimize the energy.

Example (somehow trivial but useful):

Consider the non-interacting $U = 0$ infinite chain of H atoms and an equal number of \uparrow and \downarrow electrons so that the filling factors are

$$\nu_{\uparrow} = \nu_{\downarrow} = n$$

The total energy (per site) is uniquely defined by n (average spin occupation per site). In fact:

$$n = \int_{-\infty}^{E_F} d(E) dE$$

$$e_{\text{GS}} = \int_{-\infty}^{E_F} d(E) E dE$$

One can show that

$$e_{\text{GS}} = 2n\epsilon_0 + \frac{4\gamma}{\pi} \sin(n\pi)$$

The crucial point is that this is possible for the interacting case as well. The statement is:

1. The central quantity of the theory is the site occupation

$$n_{\nu\sigma} = \langle \Psi | \hat{n}_{\nu\sigma} | \Psi \rangle$$

2. **Theorem I:** The ground state energy and any other ground state observables are unique function of the site occupation.

$$E[\{n_{\nu\sigma}\}] = \mathcal{F}[\{n_{\nu\sigma}\}] + \sum_{\nu\sigma} \epsilon_{\nu} n_{\nu\sigma}$$

3. **Theorem II:** The site occupation that minimizes the total energy functional is the exact ground state site occupation.

$$E[\{n_{\nu\sigma}\}_{\text{GS}}] = E_{\text{GS}}$$

[O. Gunnarsson and K. Schonhammer, Phys. Rev. Lett. **56**, 1968 (1986); K. Schonhammer, O. Gunnarsson and R.M. Noack, Phys. Rev. B. **52**, 2504 (1995)]

Ab-initio Theories

Lattice DFT is just a special case of a much more general method called *ab initio* density functional theory.

It is based on the famous *Hohenberg-Kohn Theorem* [P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964)]



which says:

The ground state energy E_N of a system of N electrons (interacting!!) is a unique, universal functional of the single particle charge density $\rho(\vec{r})$

$$E_N[\rho(\vec{r})] = T[\rho(\vec{r})] + E_C[\rho(\vec{r})] + E_{ext}[\rho(\vec{r})] + E_{XC}[\rho(\vec{r})]$$

Moreover the ground state charge density $\rho_{GS}(\vec{r})$ is such that:

$$E_N[\rho_{GS}] < E_N[\rho]$$

Therefore we have:

- A universal definition of the system energy
- A variational principle

How do we do calculations in practice?

Kohn and Sham demonstrated that the search for the ground state energy and charge density can be mapped onto single-particle problem.

$$H_{KS}[\rho(\vec{r})]\psi_n = E_n\psi_n$$

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + \int \frac{e^2 \rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 \vec{r}' + V_{ext}(\vec{r}) + V_{XC}(\vec{r}) \right) \psi_n = E_n \psi_n$$

where

$$E_N = \sum_n^{\text{occupied}} E_n$$

$$\rho(\vec{r}) = \sum_n^{\text{occupied}} \psi_n(\vec{r}) \psi_n^*(\vec{r})$$

So, one has a prescription on how to do calculations:

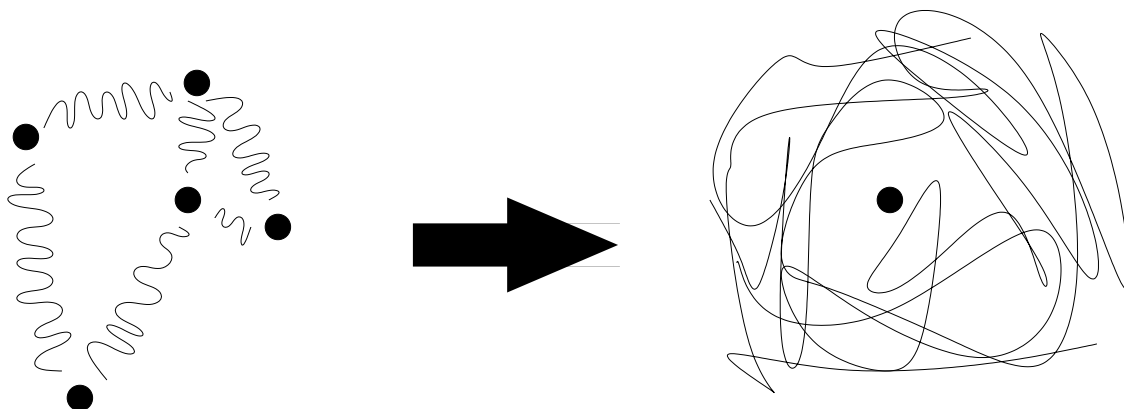
1. Create an initial charge density ρ_0
2. Define $H_{KS} = H_{KS}[\rho_0]$
3. Solve $H_{KS} \psi_n = E_n \psi_n$
4. Construct the new charge density $\rho(\vec{r}) = \sum_n^{\text{occupied}} \psi_n(\vec{r}) \psi_n^*(\vec{r})$
5. If $|\rho - \rho_0|$ is small, than stop, otherwise start again with

$$\rho_0 = \rho$$

There is only one problem V_{XC} in **NOT** known !!

However it is known for a uniform electron gas. Usually one approximates V_{XC} with the exchange- correlation potential of a uniform electron gas:

$$V_{XC}[\rho((\vec{r}))] \longrightarrow V_{XC}(\vec{r})$$



This is the Local Density Approximation (LDA).

Remarkably it works extremely well !!!!