

## 10 Self-consistent field theory

An important unsolved problem in quantum mechanics is how to deal with indistinguishable, interacting particles - in particular electrons which determine the behaviour of almost every object in nature. The basic problem is that if particles interact, that interaction must be in the Hamiltonian. So until we know where the particles are, we can't write down the Hamiltonian, but until we know the Hamiltonian, we can't tell where the particles are.

### 10.1 Hartree-Fock theory

The idea is to solve the Schroedinger equation for an electron moving in the potential of the nucleus and all the other electrons. We start with a guess for the trial electron charge density, solve  $Z/2$  one-particle Schroedinger equations (initially identical) to obtain  $Z$  electron wavefunctions. Then we construct the potential for each wavefunction from that of the nucleus and that of all the other electrons, symmetrise it, and solve the  $Z/2$  Schroedinger equations again.

Fock improved on Hartree's method by using the properly antisymmetrised wavefunction (Slater determinant) instead of simple one-electron wavefunctions. Without this, the exchange interaction is missing. This method is ideal for a computer, because it is easily written as an algorithm.

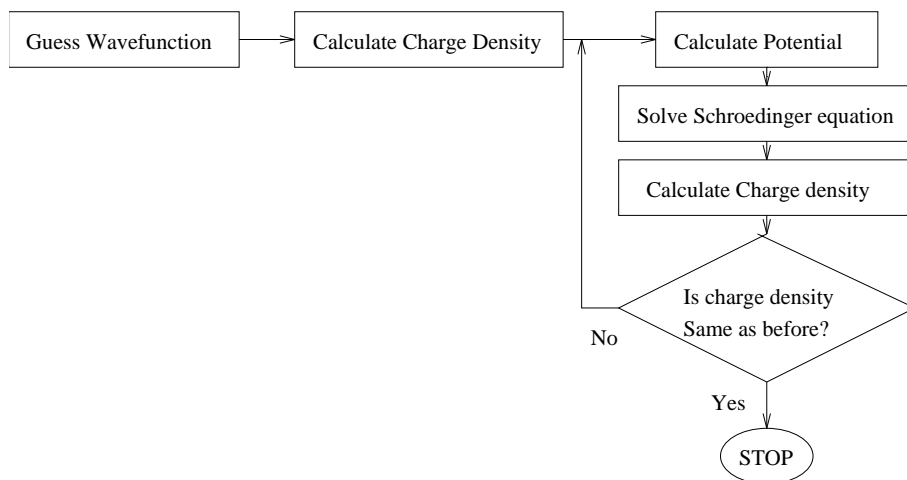


Figure 5: Algorithm for Self-consistent field theory.

Although we are concerned here with atoms, the same methodology is used for molecules or even solids (with appropriate potential symmetries and boundary conditions). This is a variational method, so wherever we refer to wavefunctions, we assume that they are expanded in some appropriate basis set.

The full set of equations are

$$\epsilon_i \psi_i(\mathbf{r}) = \left( -\frac{1}{2} \nabla^2 + V_{ion}(\mathbf{r}) \right) \psi_i(\mathbf{r}) + \sum_j \int d\mathbf{r}' \frac{|\psi_j(\mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \psi_i(\mathbf{r}) - \sum_j \delta_{\sigma_i \sigma_j} \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_j(\mathbf{r}) \quad (3)$$

The first term is the kinetic energy and electron-ion potential. The second ‘‘Hartree’’ term, is the electrostatic potential from the charge distribution of  $N$  electrons, including an unphysical self-interaction of electrons when  $j = i$ . The third, ‘‘exchange’’ term, acts only on electrons with the same spin and comes from the Slater determinant form of the wavefunction.

Physically, the effect of exchange is for like-spin electrons to avoid each other. Each electron is surrounded by an ‘‘exchange hole’’: there is one fewer like-spin electrons nearby than the mean-field would imply. The term  $i = j$  neatly cancels out the self interaction of the electron.

## 10.2 Self-consistent fields

Iterative, self-consistent approaches similar to the Hartree-Fock method can be used to calculate properties of atoms, solids or molecules. All that changes is  $V_{ion}$ .

For non-central potentials appropriate boundary conditions are needed (e.g. periodic in the case of crystals). One of the main problems now is to select an appropriate basis set for the problem. Various options exist: Plane waves, atomic orbitals, ‘augmented’ plane waves which wiggle more near to the nuclei, gaussian or ‘muffin tin’ orbitals which are localised on the nuclei. There is still a huge amount of research going on in this area.

## 10.3 Correlation: conditional probability

Hartree-Fock theory does not properly describe correlation. In the Copenhagen Interpretation, the squared modulus of the wavefunction gives the probability of finding a particle in a given place. The many-body wave function gives the N-particle distribution function, i.e.  $|\Phi(r_1, \dots, r_N)|^2$  is the probability density that particle 1 is at  $\mathbf{r}_1$ , ..., and particle N is at  $\mathbf{r}_N$ .

But when trying to work out the interaction between electrons, what we want to know is the probability of finding an electron at  $\mathbf{r}$ , *given the positions of all the other electrons*  $\{\mathbf{r}_i\}$ . This implies that the electron behaves quantum mechanically when we evaluate its wavefunction, but as a classical point particle when it contributes to the potential seen by the other electrons.

## 10.4 Lattice methods: Variational method by computer

The variational method transposes the problem of solving a differential equation onto the problem of minimising a function of many variables. It is therefore good for use with computers.

One of the simplest ways of solving for the ground state of a system with a computer is to use a basis set consisting of the values of  $|\phi\rangle$  defined on a lattice. In 1D such a solution is simply a histogram where we adjust the wavefunction at each point until the energy of the whole system is minimised. The kinetic energy (second derivative of the wavefunction) must then be obtained by some interpolation method. The weights of  $|\phi\rangle$  at each point can be regarded as a basis set. It is not complete, but it becomes more and more complete as the lattice gets finer.

Another common way of solving the Schroedinger equation numerically is to write the wavefunction as a Fourier series.

$$\Phi(\mathbf{b}) = \sum_{\mathbf{b}} a_{\mathbf{b}} e^{i\mathbf{b}\cdot\mathbf{r}}$$

where  $a_{\mathbf{b}}$  are the variational parameters. Using Fourier series (also called plane wave expansions) has several advantages. Increasing accuracy can be obtained by adding more Fourier components (because each plane wave is orthogonal to all the others), the value of  $\Phi(\mathbf{r})$  can be quickly found by a Fourier transform of  $a(\mathbf{k})$  and the kinetic energy has particularly simple form because

$$\frac{-\hbar^2 \int \Phi^* \nabla^2 \Phi d^3\mathbf{r}}{2m \int \Phi^* \Phi d^3\mathbf{r}} = \frac{\sum_{\mathbf{b}} a_{\mathbf{b}}^2 \frac{\hbar^2 b^2}{2m}}{\sum_{\mathbf{b}} a_{\mathbf{b}}^2}$$

which requires no numerical differentiation if used on a computer. The wavefunctions must be normalised, e.g. with Periodic Boundary Conditions. For a periodically repeating crystal, these are exactly the correct boundary conditions anyway. In condensed matter physics plane waves contrast with using LCAO as basis functions.

## 10.5 Pseudopotentials

A drawback to using plane waves is that electron wavefunctions don't actually look much like plane waves, so the basis set is very different from the wavefunctions, and very many Fourier

components are required. One way around this is to use a ‘pseudopotential’ which attempts to describe the potential due to the nucleus and tightly bound shells of ‘core’ electrons which do not take part in bonding. In silicon for example the pseudopotential describes the nucleus and the  $1s2s2p$  electrons.

The pseudopotential can be deduced from properties of the perfect atom: Consider:

$$V(r)\Phi(\mathbf{r}) = E + \frac{\hbar^2 \nabla^2}{2m} \Phi(\mathbf{r})$$

Where we know atomic properties  $E$  and  $\Phi(r)$ , but not  $V(r)$ , the potential seen by the outer electrons. We can invert the Schroedinger problem, solving for  $V(r)$  to give the exact  $\Phi(r)$  outside some core radius  $r > r_c$ , but smoothing it out for  $r < r_c$ .

In most applications involving chemical binding, the wavefunction only changes in the region outside  $r_c$ . So although the pseudowavefunction is not the correct Kohn-Sham eigenfunction, changes in its energy due to interaction with other electrons and ions are the same as the change in the Kohn-Sham eigenfunction.

Choosing  $r_c$  and inverting the Schroedinger equation is non-unique, but in general:

Pseudopotentials depend on the  $l$  quantum number, because they must include the fact that, e.g.  $3s$  must be radially orthogonal to  $1s$  and  $2s$ , while  $3d$  are automatically so because of the angular dependence. This is called non-locality.

The core charge produced by the pseudo wavefunctions must be the same as that produced by the atomic wavefunctions. This ensures that the pseudo atom produces the same scattering properties as the ionic core.

Pseudo-electron eigenvalues must be the same as the valence eigenvalues obtained from the atomic wavefunctions.

Pseudo wavefunctions must be continuous at the core radius as well as its first and second derivative and also be non-oscillatory.

If you find it surprising that this works - it is! However tens of thousands of calculations give energies correct to within a few percent, so the approach seems to accord well with reality.

## 10.6 k-point sampling

DFT reduces the problem of  $10^{26}$  interacting electrons to  $10^{26}$  noninteracting quasiparticles. To reduce this to a manageable number, we recall that electrons in solids can be labelled by a wavevector  $\mathbf{k}$ , and that they form bands in which electrons with similar  $\mathbf{k}$  have similar energy. The energy is the integral of these, thus we can obtain a good estimate by sampling states from an evenly-spaced grid of “ $\mathbf{k}$ -points”. As this grid becomes finer, so the accuracy of the integral improves. For most systems a surprisingly small number suffices: tens for insulators and hundreds for metals.

According to the Bloch theorem, any wavefunction must be written:

$$\Phi_{\mathbf{k}} = u(\mathbf{r}) \exp -i\mathbf{k} \cdot \mathbf{r}$$

If the wavefunction is expanded in plane waves, then

$$\Phi_{\mathbf{k}} = \sum_{\mathbf{b}} \exp -i(\mathbf{k} + \mathbf{b}) \cdot \mathbf{r}$$

where  $k$  correspond to Bloch waves longer than the unit cell, and  $b$  to basis function plane waves shorter than the cell (i.e.  $b > k$ ).

## 10.7 A continuum of quantum states: quantum numbers in a crystal

In a crystal quantum states can be indexed by the Bloch quantum number  $k$ . In the LCAO approximation, there is a state for each possible atomic orbital at each value of  $\mathbf{k}$ . As the number of electrons tends to infinity, the allowed  $\mathbf{k}$ 's form a continuum. The most important application of quantum mechanics in solid state physics is to understand the relationship between energy and momentum. A graph of energy vs momentum is called a band structure.

States are occupied from the lowest energy upwards according to the exclusion principle. The set of momenta which correspond to the maximum allowed energy form a surface in the 3-d space - the so-called Fermi Surface.

Shown is the valence “band structure” of dhcp potassium calculated using DFT and pseudopotentials: letters are crystallographic notation for values of  $\mathbf{k}$  ( $\Gamma = (0, 0, 0)$ , others are on the edge of the Brillouin zone). Note the free electron parabola around  $\Gamma$ , as  $E = \hbar^2 k^2 / 2m$ . This structure has four layers of atoms per unit cell, so *on average* there are two bands below the Fermi surface at each  $k$ -point (each is spin degenerate). There are lots of bands crossing the Fermi level, showing that electrons can move from one state to another without requiring energy: potassium is a metal.  $\Gamma$ -A is quite a short distance in  $k$ -space, corresponding to waves along the long direction in the unit cell: the band structure appears like a parabola “folded back” on itself.

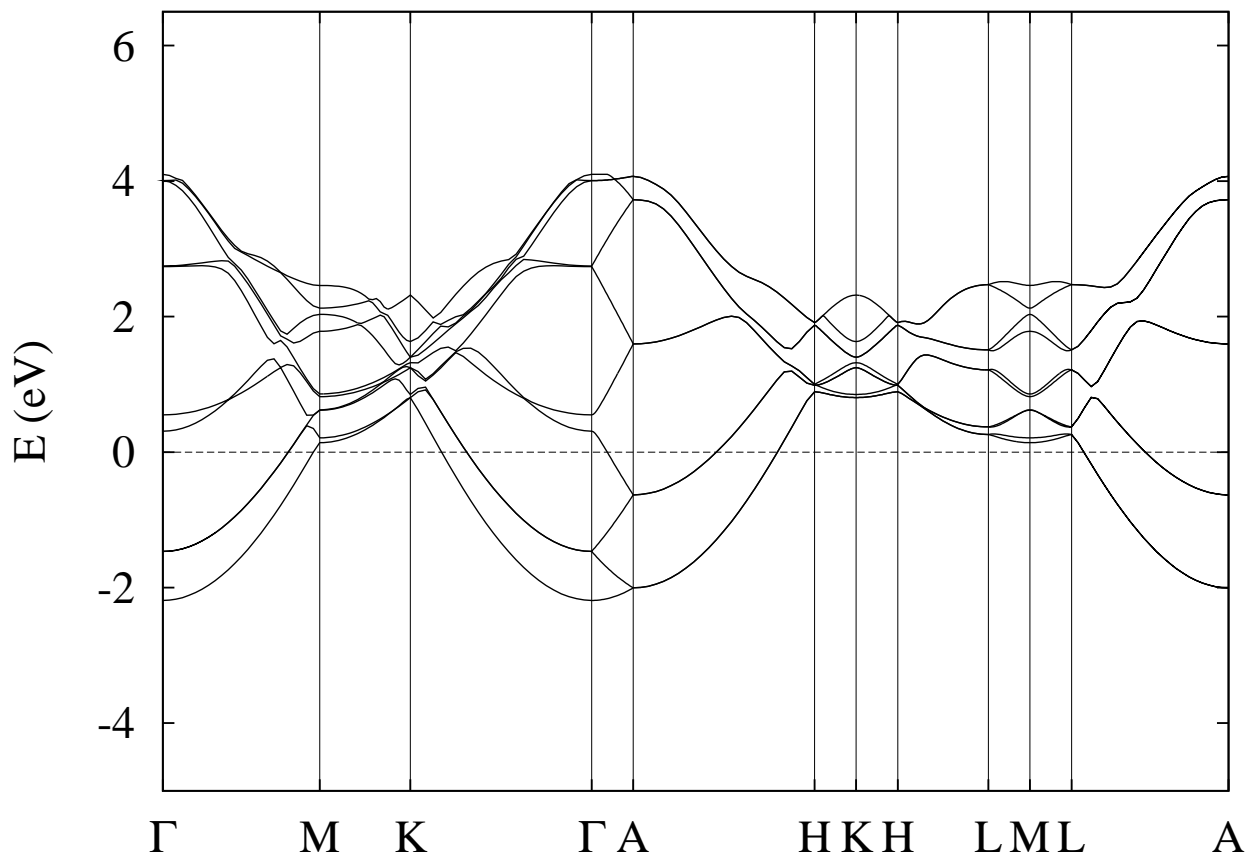


Figure 6: Band structure of potassium, energy scaled so that  $E_F=0$ . x-axis labels denote a path through the 3d space of  $\mathbf{k}$ -vectors.