Phys 5870: Modern Computational Methods in Solids

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January 5, 2012

1 Schödinger's Equation

According to the fourth postulate of quantum mechanics, the time evolution of the state function $\psi(x,t)$ is determined by the so-called *time dependent Schrödinger's equation*:

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{x},t) = H\psi(\mathbf{x},t). \tag{1}$$

The operator H is the Hamiltonian of the system. If H is time-independent, we can separate this equatioon into spatial and time-dependent components:

$$\psi(\mathbf{x},t) = \phi(\mathbf{x})\chi(t). \tag{2}$$

By substituting into (1), we obtain:

$$i\hbar\frac{\partial\chi/t}{\chi} = \frac{H\phi}{\phi}. \tag{3}$$

This equation is satisfied if both sides are equal to a constant, that we call E:

$$H\phi(\mathbf{x}) = \phi(\mathbf{x}) \tag{4}$$

$$(\frac{\partial}{\partial t} + \frac{iE}{\hbar})\chi(t) = 0 \tag{5}$$

The first of these equations is the *time-independent or stationary Schödinger's equation*. As we can see, E is an eigenvalue of H, and therefore we conclude that E is the energy of the system.

The second equation is simply solved to give us the oscillating form

$$\chi(t) = A \exp\,(\frac{-iEt}{\hbar}) \tag{6}$$

Suppose that we solve the time-independent Schödinger's equation and obtain the eigenvalues and eigenfunctions

$$H\phi_n = E_n\phi_n, \tag{7}$$

For each such solution there is a corresponding solution to the time-dependent Schödinger's equation

$$\psi_n(\mathbf{x}, t) = A\phi_n(\mathbf{x}) \exp\,(-\frac{iE_nt}{\hbar}). \tag{8}$$

In cases with a discrete set of solutions, such as in a finite system, the subindex n is an integer. In cases where one obtains a continuum of solutions, we typically use the letter k. For instance, in the case of a free particle in one dimension we have:

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2. \tag{9}$$

The time-independent Schrödinger's solution becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\phi(x) = E\phi(x). \tag{10}$$

The corresponding free-particle solutions are given by

$$\phi_k(x) = A\exp(ikx), \tag{11}$$

with eigenvalue (energy)

$$E_k = \frac{\hbar^2k^2}{2m} = \frac{p^2}{2m}, \tag{12}$$

where the momentum of the particle is $p = \hbar^2k^2$.

The solution to the time-dependent Schrödinger's equation will be given by

$$\phi_k(x, t) = A\exp i(kx - \omega t), \tag{13}$$

where we have labeled

$$\hbar\omega = E_k. \tag{14}$$

2 Variational Methods

The variational method is an approximate method used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it is hard to determine a good unperturbed Hamiltonian (i.e., one which makes the perturbation small but is still solvable). On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.

The basic idea of the variational method is to guess a “trial” wavefunction for the problem, which consists of some adjustable parameters called “variational parameters.” These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wavefunction and its corresponding energy are variational method approximations to the exact wavefunction and energy.

Why would it make sense that the best approximate trial wavefunction is the one with the lowest energy? This results from the Variational Theorem, which states that the energy of any trial wavefunction E is always an upper bound to the exact ground state energy E_0. This can be proven easily. Let the trial wavefunction be denoted ϕ. Any trial function can formally be expanded as a linear combination of the exact eigenfunctions ψ_i. Of course, in practice, we do not know the ψ_i, since we are assuming that we are applying the variational method to a problem we can not solve analytically. Nevertheless, that does not prevent us from using the exact eigenfunctions in our proof, since they certainly exist and form a complete set, even if we do not happen to know them:

$$\sum_{i,j} \langle \psi_i | \psi_j \rangle = \delta_{i,j} \tag{15}$$

where $\delta_{i,j}$ is the Kronecker delta.

$$H \left| \psi_i \right\rangle = E_i \left| \psi_i \right\rangle . \tag{16}$$

We are asuming that the physical states are normalized, *i.e.* their norm is equal to unity (we can always make it to do so). Let us assume that we have a candidate wavefunction to describe the ground-state, that we call $|\phi\rangle$, and that this function deppends on a set of parameters c_i, that we call *variational parameters* and are complex numbers. Ignoring complications involved with a continuous spectrum of H, suppose that the spectrum is bounded from below and that its greatest lower bound is E_0. So, the approximate energy corresponding to this wavefunction is the expectation value of H:

$$\begin{aligned}\langle\phi|H|\phi\rangle &= \sum_{i,j}\langle\phi|\psi_i\rangle\langle\psi_i|H|\psi_j\rangle\langle\psi_j|\phi\rangle &(17)\\ &= \sum_i E_i\,|\langle\psi_i|\phi\rangle|^2 \geq \sum_i E_0\,|\langle\psi_i|\phi\rangle|^2 = E_0 &(18)\end{aligned}$$

In other words, the energy of any approximate wavefunction is always greater than or equal to the exact ground state energy E_0. This explains the strategy of the variational method: since the energy of any approximate trial function is always above the true energy, then any variations in the trial function which lower its energy are necessarily making the approximate energy closer to the exact answer. (The trial wavefunction is also a better approximation to the true ground state wavefunction as the energy is lowered, although not necessarily in every possible sense unless the limit $\phi = \psi_0$ is reached).

Frequently, the trial function is written as a linear combination of basis functions, such as

$$|\phi\rangle = \sum_i c_i|\phi_i\rangle.$$

This leads to the linear variation method, and the variational parameters are the expansion coefficients c_i. We shall assume that the possible solutions are restricted to a subspace of the Hilbert space, and we shall seek the best possible solution in this subspace.

The energy for this approximate wavefunction is just

$$E[\phi] = \frac{\sum_{ij} c_i^* c_j\langle\phi_i|H|\phi_j\rangle}{\sum_{ij} c_i^* c_j\langle\phi_i|\phi_j\rangle}, \tag{19}$$

which can be simplified using the notation $H_{ij} = \langle\psi_i|H|\psi_j\rangle = \int\phi_i^* H\phi_j$, $S_{ij} = \langle\psi_i|H|\psi_j\rangle = \int\phi_i^*\phi_j$, to yield

$$E[\phi] = \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j S_{ij}}.$$

In order to find the optimial solution, we need to minimize this energy functional with respect to the variational parameters c_i, or calculate the variation such that:

$$\delta E(c_i) = 0. \tag{20}$$

We will calculate only the variation with respect to c_i^*, since the variation with respect to c_j will yield the same result:

$$\delta E \;=\; \sum_i \frac{\left(\sum_j c_j H_{ij} \sum_{i',j'} c^*_{i'} c_{j'} S_{i'j'} - \sum_j c_j S_{ij} \sum_{i',j'} c^*_{i'} c_{j'} H_{i'j'}\right)}{\left(\sum_{i',j'} c^*_{i'} c_{j'} S_{i'j'}\right)^2} \delta c_i^*. \quad (21)$$

Reordering some terms we can rewrite it as:

$$\sum_i \left(\frac{\sum_j c_j H_{ij} - E \sum_j c_j S_{ij}}{\sum_{i'j'} c^*_{i'} c_{j'} S_{i'j'}} \right) \delta c_i^*, \quad (22)$$

where E is given by Eq.(19). This should be satisfied for all c_i's, and we find that the coefficients should satisfy the following conditions:

$$\sum_{j=1}^{N} (H_{ij} - E S_{ij}) c_j = 0 \quad i = 1, 2, ..., N. \quad (23)$$

This is a generalized eigenvalue problem, that can be rewritten:

$$\mathbf{H}\mathbf{c} = E\mathbf{S}\mathbf{c}, \quad (24)$$

where **H** is the Hamiltonian matrix, and **S** is the so-called "overlap matrix". The main difference with an ordinary eigenvalue problem is the marix **S** on the right hand side. We'll see how to solve this problem in the exercises. The solution to thsi problem is obtained by solving the following "secular determinant"

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1N} - ES_{1N} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2N} - ES_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ H_{N1} - ES_{N1} & H_{2N} - ES_{2N} & \cdots & H_{NN} - ES_{NN} \end{vmatrix} = 0. \quad (25)$$

If an orthonormal basis is used, the secular equation is greatly simplified because $S_{ij} = \delta_{ij}$ (1 for $i = j$ and 0 for $i \neq j$), and we obtain:

$$\mathbf{H}\mathbf{c} = E\mathbf{c}, \quad (26)$$

which is nothing else but the stationary Schrödinger's equation, formulated in this basis. In this case, the secular determinant is

$$\begin{vmatrix} H_{11}-E & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22}-E & \cdots & H_{2N} \\ \vdots & \vdots & \vdots & \vdots \\ H_{N1} & H_{2N} & \cdots & H_{NN}-E \end{vmatrix} = 0, \tag{27}$$

In either case, the secular determinant for N basis functions gives an N-th order polynomial in E which is solved for N different roots, each of which approximates a different eigenvalue. These equations can be easily solved using readily available library routines, such as those in Numerical Recipes, or Lapack. At this point one may wonder where the approximation is: aren't we solving the problem exactly? If we take into account a complete basis set, the answer is "yes, we are solving the problem exactly". But as we said before, teh Hilbert space is very large, and we therefore have to limit the basis size to a number that is easily tractable with a computer. Therefore, we have to work in a constrained Hilbert space with a relatively small number of basis states kept, which makes the result variational. Because of the computer time needed for numerical diagonalizations scales as the third power of the linear matrix size, we would want to keep the basis size as small as possible. Therefore, the basis wavefunctions must be choses carefully: it should be possible to approximate the exact solution to the full problem with a small number of basis states. Inorder to do that, we need some good intuition about the underlying physics of the problem.

We have used a linear parametrization of the wave function. This greatly simplifies the calculations. However, nonlinear parametrizations are also possible, such as in the case of hartree-Fock theory.

The variational method lies behind hartree-Fock theory and the configuration interaction method for the electronic structure of atoms and molecules, as we will see in the following chapter.

2.1 Examples of linear variational calculations

2.1.1 The infinite potential well

The potential well with inifinite barriers is defined:

$$V(x) = \begin{cases} \infty & \text{for} \quad |x| > |a| \\ 0 & \text{for} \quad |x| \leq |a| \end{cases} \tag{28}$$

and it forces the wave function to vanish at the boundaries of the well at $x = \pm a$. The exact solutioon for this problems is known and treated in introductory quantum mechanics courses. Here we discuss a linear variational approach to be compared with the exact solution. We take $a = 1$ and use natural units such that $\hbar^2/2m = 1$.

As basis functions we take simple polynomials that vanish on the boundaries of the well:

$$\psi_n(x) = x^n(x-1)(x+1), n = 0, 1, 2, 3... \tag{29}$$

The reason for choosing this particular form of basis functions is that the relevant matrix elements can easily be calculated analytically. We start we the overlap matrix:

$$S_{mn} = \langle \psi_n | \psi_m \rangle = \int_{-1}^{1} \psi_n(x) \psi_m(x) dx. \tag{30}$$

Working out the integrals, one obtains

$$S_{mn} = \frac{2}{n+m+5} - \frac{4}{n+m+3} + \frac{2}{n+m+1} \tag{31}$$

for $n + m$ even, and zero otherwise.

We can also calculate the Hamiltonian matrix elements:

$$H_{mn} = \langle \psi_n | p^2 | \psi_m \rangle = \int_{-1}^{1} \psi_n(x) \left(-\frac{d^2}{dx^2} \right) \psi_m(x) dx \tag{32}$$

$$= -8 \left[\frac{1 - m - n - 2mn}{(m+n+3)(m+n+1)(m+n-1)} \right] \tag{33}$$

for $m + n$ even, and zero otherwise.

Exercise 2.1: Infinite potential well

• Write a computer program in which you fill the overlap and Hamiltonian matrices for this problem. Use standard software to solve the generalized eigenvalue problem. Notice that the matrices are Hermitian, so only the upper, or lower triangular parts have to be calculated (including the diagonal).
• Compare results with exact analytic solutions. These are given by

$$\psi_n(x) = \begin{cases} \cos(k_n x) & n \quad \text{odd} \\ \sin(k_n x) & n \quad \text{even and positive} \end{cases} \tag{34}$$

with $k_n = n\pi/2, n = 1, 2...$, and the corresponding energies are given by

$$E_n = k_n^2 = \frac{n^2\pi^2}{4} \tag{35}$$

For each eigenvector $\mathbf{c}$, the function $\sum_{p=1}^{N} = c_p\phi_p(x)$ should approximate an exact eigenfunction. They can be compared by displaying both graphically. Carry out the comparison for various numbers of basis states kept.

2.1.2 Hydrogen atom

One example of the variational method would be using the Gaussian function $\chi(r) = e^{-\alpha r^2}$ as a trial function for the hydrogen atom ground state. This problem could be solved by the variational method by obtaining the energy of $\chi(r)$ as a function of the variational parameter α, and then minimizing $E(\alpha)$ to find the optimum value α_{min}. The variational theorem's approximate wavefunction and energy for the hydrogen atom would then be $\chi(r) = e^{-\alpha_{min} r^2}$ and $E(\alpha_{min})$.

This is a one electron problem, so we do not have to worry about electron-electron interactions, or antisymmetrization of the wave function. The Schrödinger's equation reads:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\right]\psi(x) = E\psi(x) \tag{36}$$

where the second term is the Coulomb interaction with the positive nucleus (remember, this is a charged particle in a central potential). The mass m is the reduced mass of the proton-electron system, which is approximately equal to the electron mass. The ground state has energy

$$E = -\frac{N}{\hbar^2}\left(\frac{\mathrm{e}^2}{4\pi\epsilon_0}\right)^2 \approx -13.6058\mathrm{eV} \tag{37}$$

and the wave function is given by

$$\psi(\mathbf{x}) = \frac{2}{a_0^{3/2}}\exp\left(-x/a_0\right) \tag{38}$$

where a_0 is Bohr's radius

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m\mathrm{e}^2}. \tag{39}$$

It is convenient to use units such that equations take on a simpler form. These are the so-called *standard units* in electronic structure: the unit of distance is Bohr's radius, masses are expressed in units of the electon mass m_e, and charge in units of the electron charge e. The energy is finally given in "hartrees", equal to $E_H = m_\mathrm{e}c^2\alpha^2$ (where α is the fine structure constant). In these units the Schrödinger equation for the hydrogen atom assumes the following simpler form:

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\psi(x) = E\psi(x). \tag{40}$$

To approximate the ground state energy and wave function of the hydrogen atom in a linear variational procedure, we will use Gaussian basis functions. For the ground state, we only need angular momentum $l = 0$ wave functions (s-orbitals), which have the form:

$$\chi_p(r) = \exp\left(-\alpha_p r^2\right) \tag{41}$$

centered on the nucleus (whis is thus placed at the origin). We have to specify the values of the exponents α_p, which are our variational parameters. Optimal values of these exponents have been previously found by other means, and in our case, we will keep these values fixed:

$$\alpha_1 = 13.00773 \tag{42}$$

$$\alpha_2 = 1.962079 \tag{43}$$

$$\alpha_3 = 0.444529 \tag{44}$$

$$\alpha_4 = 0.1219492. \tag{45}$$

If the program works correctly, it should shield a value of the energy close to the exact results $E_0 = -1/2E_H$.

It remains to determine the coefficients of the linear expansion, by solving the generalized eigenvalue problem, as we did in the previous example. The matrix elements of the overlap matrix $\mathbf{S}$, the kinetic energy matrix $\mathbf{T}$, and the Coulomb interaction $\mathbf{V}$ are given by:

$$S_{pq} = \int d^3r e^{-\alpha_p r^2} e^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q}\right)^{3/2} \tag{46}$$

$$T_{pq} = \int d^3r e^{-\alpha_p r^2} \nabla^2 e^{-\alpha_q r^2} = 3\frac{\alpha_p \alpha_q \pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}} \tag{47}$$

$$V_{pq} = \int d^3r e^{-\alpha_p r^2} \frac{1}{r} e^{-\alpha_q r^2} = -\frac{2\pi}{(\alpha_p + \alpha_q)}. \tag{48}$$

Using these expressions, one can fill the overlap and Hamiltonian matrices and solve the problem numerically.

Exercise 2.2: Hydrogen atom

• Solve the problem stated in the previous section. If your program has no errors, you should obtain $E = -0.499278E_H$, which is remarkable considering that only four basis states have been taken into account.
• Compare graphically the variational ground-state to the exact one, given by Eq.(38).

3 The Hartree-Fock method

In the previous section we have seen how to apply the variational method to a simple simgle-particle problem. As we treat more complicated problems, such as heavier atoms, molecules, and ultimately, solids, the complexitiy increases as the number of particles, and degrees of freedom increases. In these so-called, many-body problems, we have to consider the motion of the nuclei, the interaction between the protons and electrons, and between electrons themselves. We will consider a general system of N nuclei described by coordinates, $\mathbf{R}_1, ..., \mathbf{R}_N \equiv \mathbf{R}$, momenta, $\mathbf{P}_1, ..., \mathbf{P}_N \equiv \mathbf{P}$, and masses $M_1, ..., M_N$, and N_e electrons described by coordinates, $\mathbf{r}_1, ..., \mathbf{r}_{N_e} \equiv \mathbf{r}$, momenta, $\mathbf{p}_1, ..., \mathbf{p}_{N_e} \equiv \mathbf{p}$, and spin variables, $s_1, ..., s_{N_e} \equiv s$. The Hamiltonian of the system is given by

$$H = T_N(\mathbf{R}) + T_e(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}),$$

where T_N is the kinetic energy of the nuclei, T_e is the kinetic energy of the electrons, and V_{NN}, V_{eN} and V_{ee} contain the nucleus-nucleus, nuclei-electron, and electron-electron interactions, respectively:

$$\begin{aligned}
T_N &= \sum_{I=1}^{N} \frac{\mathbf{P}_I^2}{2M_I}, && (49)\\
T_e &= \sum_{i=1}^{N_e} \frac{\mathbf{p}_i^2}{2m_I}, && (50)\\
V_{NN} &= \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} = \sum_{I>J} \frac{Z_I Z_J e^2}{r_{IJ}}, && (51)\\
V_{eN} &= -\sum_{i,I} \frac{Z_I e^2}{|\mathbf{R}_I - \mathbf{r}_i|} = -\sum_{I>J} \frac{Z_I e^2}{r_{Ii}}, && (52)\\
V_{ee} &= \sum_{i,j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_i|} = -\sum_{i>j} \frac{e^2}{r_{ij}}. && (53)\\
& && (54)
\end{aligned}$$

This is sometimes jokingly referred to as the "equation of everything". Clearly,if we could solve this problem, condensed matter would be a dead field. "Luckily" for us, this equation is extremely complicated, and basically intractable. Therefore, we are forced to make several approximations. The first one is to assume that the nuclei are static. This is justified when when realizes that the mass of the protons and neutrons is much larger that the mass of the electrons by three orders of magnitude. Therefore the time scale for motion of the nuclei is much large than the one for the electrons, that move at much faster speeds. This approach is the so-called Born-Oppenheimer approximation: by taking the position of the nuclei fixed, the main remaining problem is the electronic part.

A second approximation is to assume that the wave-function of the many-electron system takes the form of an antisymmetized product of one-electron wave-functions (remember that electrons are fermions). This simplification transforms the complicated many-body problem into the problem of a single-particle in an effective "mean-field" potential determined by the positions of the other electrons. This is the basic idea behind the Hartree-Fock method.

We can immediatley make two obervations: The first is that we are assuming that the physics can be described by single-particle wave-functions, and therefore, thsi corresponds to approximating the actual ground state by a *variational* ansatz. As a consequence, all the concepts learned in the previous section will apply here as well. A second observation is that the effective potential feld by the electrons will have to be calculated self-consistently: every time we update or modify the single particle wave-function, the potential will have to be updated as well.

We shall see that in this variational approach, correlations between electrons are neglected to some extent. In particular, Coulomb repulsion between electrons is taken into account in an averaged way.

3.1 The Born-Oppenheimer approximation

The Born-Oppenheimer Approximation is the assumption that the electronic motion and the nuclear motion in molecules can be separated. It leads to a molecular wave function in terms of electron positions and nuclear positions.

This involves the following assumptions:

- The electronic wavefunction depends upon the nuclear positions but not upon their velocities, i.e., the nuclear motion is so much slower than electron motion that they can be considered to be fixed.
- The nuclear motion (e.g., rotation, vibration) sees a smeared out potential from the speedy electrons.

We know that if a Hamiltonian is separable into two or more terms, then the total eigenfunctions are products of the individual eigenfunctions of the separated Hamiltonian terms, and the total eigenvalues are sums of individual eigenvalues of the separated Hamiltonian terms.

Consider, for example, a Hamiltonian which is separable into two terms, one involving coordinate q_1 and the other involving coordinate q_2.

$$H = H_1(q_1) + H_2(q_2)$$

with the overall Schrdinger equation being

$$H\psi(q_1, q_2) = E\psi(q_1, q_2)$$

If we assume that the total wavefunction can be written in the form $\psi(q_1, q_2) = \psi_1(q_1)\psi_2(q_2)$, where $\psi_1(q_1)$ and $\psi_2(q_2)$ are eigenfunctions of H_1 and H_2 with eigenvalues E_1 and E_2, then

$$\begin{aligned} H\psi(q_1, q_2) &= (H_1 + H_2)\psi_1(q_1)\psi_2(q_2) && (55) \\ &= H_1\psi_1(q_1)\psi_2(q_2) + H_2\psi_1(q_1)\psi_2(q_2) && (56) \\ &= E_1\psi_1(q_1)\psi_2(q_2) + E_2\psi_1(q_1)\psi_2(q_2) && (57) \\ &= (E_1 + E_2)\psi_1(q_1)\psi_2(q_2) && (58) \\ &= E\psi(q_1, q_2) && (59) \end{aligned}$$

Thus the eigenfunctions of H are products of the eigenfunctions of H_1 and H_2, and the eigenvalues are the sums of eigenvalues of H_1 and H_2.

Going back to our original problem, Eq.(3), , we would start by seeking the eigenfunctions and eigenvalues of this Hamiltonian, which will be given by solution of the time-independent Schrödinger equation

$$\left[T_N + T_e + V_{ee}(\mathbf{r}) + V_{NN}(\mathbf{R}) + V_{eN}(\mathbf{r}, \mathbf{R})\right]\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}).$$

We first invoke the Born-Oppenheimer approximation by recognizing that, in a dynamical sense, there is a strong separation of time scales between the electronic and nuclear motion, since the electrons are lighter than the nuclei by three orders of magnitude. This can be exploited by assuming a quasi-separable ansatz of the form

$$\Psi(\mathbf{x}, \mathbf{R}) = \phi_e(\mathbf{x}, \mathbf{R})\phi_N(\mathbf{R})$$

where $\phi_N(\mathbf{R})$ is a nuclear wave function and $\phi_e(\mathbf{x}, \mathbf{R})$ is an electronic wave function that depends parametrically on the nuclear positions. If we look again at the Hamiltonian, we would notice right away that the term V_eN would prevent us from applying this separation of variables. The Born-Oppenheimer (named for its original inventors, Max Born and Robert Oppenheimer) is based on the fact that nuclei are several thousand times heavier than electrons. The proton, itself, is approximately 2000 times more massive than an electron. In a dynamical sense, the electrons can be regarded as particles that follow the nuclear motion adiabatically, meaning that they are "dragged" along with the nuclei without requiring a finite relaxation time. This, of course, is an approximation, since there could be non-adiabatic effects that do not allow the electrons to follow in this "instantaneous" manner, however, in many systems, the adiabatic separation between electrons and nuclei is an excellent approximation. Another consequence of the mass difference between electrons and nuclei is that the nuclear components of the wave function are spatially more localized than the electronic component of the wave function. In the classical limit, the nuclear are fully localized about single points representing classical point particles.

After these considerations, $H_N(\mathbf{R})$ can be neglected since T_N is smaller than T_e by a factor of M/m. Thus for a fixed nuclear configuration, we have

$$H_{el} = T_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{NN}(\mathbf{R}) + V_{ee}(\mathbf{r})$$

such that

$$H_{el}\phi_e(\mathbf{r}, \mathbf{R}) = E_{el}\phi_e(\mathbf{r}, \mathbf{R})$$

This is the "clamped-nuclei" Schrödinger equation. Quite frequently $V_{NN}(\mathbf{R})$ is neglected in the above equation, which is justified since in this case $\mathbf{R}$ is just a parameter so that $V_{NN}(\mathbf{R})$ is just a constant and shifts the eigenvalues only by some constant amount. Leaving $V_{NN}(\mathbf{R})$ out of the electronic Schrdinger equation leads to a similar equation,

$$\begin{aligned} H_e &= T_e(\mathbf{r}) + V_{eN}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) && (60) \\ H_e\phi_e(\mathbf{r}, \mathbf{R}) &= E_e\phi_e(\mathbf{r}, \mathbf{R}), && (61) \end{aligned}$$

where we have used a new subscript "e" on the electronic Hamiltonian and energy to distinguish from the case where V_{NN} is included.

We now consider again the original Hamiltonian (3). If we insert a wavefunction of the form $\Psi(\mathbf{r},\mathbf{R}) = \phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R})$, we obtain

$$H\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) \tag{62}$$

$$\{T_N(\mathbf{R}) + T_e(\mathbf{r}) + V_{eN}(\mathbf{r},\mathbf{R}) + V_{NN}(\mathbf{R})\}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) \tag{63}$$

Since T_e contains no $\mathbf{R}$ dependence,

$$T_e\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_N(\mathbf{R})T_e\phi_e(\mathbf{r},\mathbf{R})$$

However, we may not immediately assume

$$T_N\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R})$$

(this point is tacitly assumed by most introductory textbooks). By the chain rule,

$$\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}) = \phi_e(\mathbf{r},\mathbf{R})\nabla_R^2\phi_N(\mathbf{R}) + 2\nabla_R\phi_e(\mathbf{r},\mathbf{R})\nabla_R\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})$$

Using these facts, along with the electronic Schrdöinger equation,

$$\{T_e + V_{eN}(\mathbf{r},\mathbf{R}) + V_{ee}\}\phi_e(\mathbf{r},\mathbf{R}) = H_e\phi_e(\mathbf{r},\mathbf{R}) = E_e\phi_e(\mathbf{r},\mathbf{R})$$

we simplify Eq.(63) to

$$\phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\phi_e(\mathbf{r},\mathbf{R})(E_e + V_{NN}) \tag{64}$$

$$-\left\{\sum_A \frac{1}{2M}(2\nabla_R\phi_e(\mathbf{r},\mathbf{R})\nabla_R\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})\nabla_R^2\phi_e(\mathbf{r},\mathbf{R}))\right\} \tag{65}$$

$$= E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R}). \tag{66}$$

We must now estimate the magnitude of the last term in brackets. A typical contribution has the form $1/(2M)\nabla_R^2\phi_e(\mathbf{r},\mathbf{R})$, but $\nabla_R\phi_e(\mathbf{r},\mathbf{R})$ is of the same order as $\nabla_r\phi_e(\mathbf{r},\mathbf{R})$ since the derivatives operate over approximately the same dimensions. The latter is $\phi_e(\mathbf{r},\mathbf{R})p_e$, with p_e the momentum of an electron. Therefore $1/(2M)\nabla_R^2\phi_e(\mathbf{r},\mathbf{R}) \approx p_e^2/(2M) = (m/M)E_e$. Since $m/M \sim 1/10000$, the term in brackets can be dropped, giving

$$\phi_e(\mathbf{r},\mathbf{R})T_N\phi_N(\mathbf{R}) + \phi_N(\mathbf{R})E_e\phi_e(\mathbf{r},\mathbf{R}) + \phi_N(\mathbf{R})V_{NN}\phi_e(\mathbf{r},\mathbf{R}) = E_{tot}\phi_e(\mathbf{r},\mathbf{R})\phi_N(\mathbf{R})$$

$$\{T_N + E_e + V_{NN}\}\phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R}).$$

This is the nuclear Shrödinger equation we anticipated–the nuclei move in a potential set up by the electrons.

To summarize, the large difference in the relative masses of the electrons and nuclei allows us to approximately separate the wavefunction as a product of nuclear and electronic terms. The electronic wavefucntion $\phi_e(\mathbf{r}, \mathbf{R})$ is solved for a given set of nuclear coordinates,

$$H_e\phi_e(\mathbf{r}, \mathbf{R}) = \left\{ -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I}{r_{Ii}} + \sum_{i>j} \frac{1}{r_{ij}} \right\} \phi_e(\mathbf{r}, \mathbf{R}) = E_e(\mathbf{R})\phi_e(\mathbf{r}, \mathbf{R}),$$

and the electronic energy obtained contributes a potential term to the motion of the nuclei described by the nuclear wavefunction $\phi_N(\mathbf{R})$.

$$H_N\phi_N(\mathbf{R}) = \left\{ -\sum_I \frac{1}{2M_I}\nabla_I^2 + E_e(\mathbf{R}) + \sum_{I>J} \frac{Z_I Z_J}{R_{IJ}} \right\} \phi_N(\mathbf{R}) = E_{tot}\phi_N(\mathbf{R})$$

3.2 The helium atom

in this section we introduce a first application of the Hartree-Fock methos for the helium atom. In order to carry out the calculation we shall use the electronic Hamiltonian within the Born-Oppenheimer approximation.

The helium atom has two electrons, and we will label their coordinates $\mathbf{x}_x$ and $\mathbf{x}_2$, wich are combined position and spin coordinates $\mathbf{x}_i = \{\mathbf{r}_i, s_i\}$, where the spin can assume two values $s_i = \uparrow, \downarrow$. The Born-Oppenheimer Hamiltonian for the helium atom reads:

$$H = -\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \tag{67}$$

Since electrons are fermions, the wave function should be antisymmetric under an exchange of coordinates. We use the following antisymmetric trial wave function for the ground state:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) \times \frac{1}{\sqrt{2}}\left[|\uparrow\rangle_1 |\downarrow\rangle_2 - |\downarrow\rangle_1 |\uparrow\rangle_2 \right]. \tag{68}$$

We shall now replace this into the Schrödinger equation. Since the Hamiltonian does not act on the spin degree of freedom, we are left with:

$$\left[-\frac{1}{2}\nabla_{r_1}^2 - \frac{1}{2}\nabla_{r_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right] \phi(\mathbf{r}_1)\phi(\mathbf{r}_2) = E\phi(\mathbf{r}_1)\phi(\mathbf{r}_2). \tag{69}$$

We now multiply both sides from the left by $\phi(\mathbf{r}_2^*)$ and we integrate over $\mathbf{r}_2$, arriving to:

$$\left[-\frac{1}{2}\nabla^2_{r_1} - \frac{Z}{r_1} + \int d^3r_2|\phi(\mathbf{r}_2)|^2\frac{1}{|\mathbf{r}_2 - \mathbf{r}_2|}\right]\phi(\mathbf{r}_1) = E'\phi(\mathbf{r}_1), \tag{70}$$

where several integrals we have removed the constant terms that do not deppend on $\vec{r}_1$ by absorving them into E'. The third term on the left hand side can be recognized as the Coulomb energy of particle 1 in the electric field generated by the charge density of particle 2.

We now have a single-particle Hamiltonian for the wave-function of a single electron. However, the Hamiltonian deppends on the wave-function we are looking for. This is a *self-consistent* problem: ϕ is the solution to the Schrödinger equation, but the Hamiltonian deppends on ϕ itself. To solve this kind of problem, we start searching for a solution with some trial wave-function $\phi^{(0)}$, which is used for constructing the potential. SOlving the Schrödinger equation for this potential one finds a new ground state $\phi^{(1)}$, which is in turn used to build a new potential. The procedure is repeated until the ground state $\phi^{(i)}$ and the corresponding energy $E^{(i)}$ at step i do not deviate appreciably from those in the previous step.

The wave-function we have used is called *uncorrelated* because of the fact that the probability $P(\mathbf{r}_1, \mathbf{r}_2)$ for finding a particle at position $\mathbf{r}_1$ and another one at $\mathbf{r}_2$ is uncorrelated, ı.e. can be written as the product of two one-electron probabilities:

$$P(\mathbf{r}_1, \mathbf{r}_2) = P(\mathbf{r}_1)P(\mathbf{r}_2). \tag{71}$$

This does not mean that the electrons do not feel each other: in the depetrmination of the wave function, the term $1/|\mathbf{r}_1 - \mathbf{r}_2|$ was taken into account. But this was done in an average way: it is not the actual position of particle 2 that determines the wave-function for electron 1, but the average charge distribution of electron 2. This is why this approach is usually referred-to as *mean field.*

The Coulomb term in (70) is called Hartree potential. We will see that in more complex many-body problems as second term arises, due to the fermionic exchange statistics.

3.3 A program for the helium ground-state

We shall take a similar variational approach as the one used for the hydrogen atom. Let us take a wave-function of the form

$$\phi(\mathbf{r}) = \sum_{p=1}^{N} C_p \chi_p(\mathbf{r}). \tag{72}$$

Replacing into (70) we obtain

$$\left[-\frac{1}{2}\nabla^2_{r_1} - \frac{Z}{r_1} + \sum_{r,s=1}^{N} C_r C_s \int d^3 r_2 \chi_r(\mathbf{r}_2)\chi_s(\mathbf{r}_2) \frac{1}{|\mathbf{r}_2 - \mathbf{r}_2|} \right] \sum_{q=1}^{N} C_q \chi_q(\mathbf{r}_1) \tag{73}$$

$$= E' \sum_{q=1}^{N} C_q \chi_q(\mathbf{r}_1). \tag{74}$$

Note that the C_p are real as the functions χ_p are also real. Multiplying from the left by $\chi_p(\mathbf{r}_1)$ and integrating over $\mathbf{r}_1$ leads to

$$\sum_{pq} \left(h_{pq} + \sum_{rs} C_r C_s Q_{pqrs} \right) C_q = E' \sum_{pq} S_{pq} C_q \tag{75}$$

with

$$h_{pq} = \left\langle \chi_p \middle| -\frac{1}{2}\nabla^2 - \frac{Z}{r} \middle| \chi_q \right\rangle \tag{76}$$

$$Q_{pqrs} = \int d^3 r_2 d^3 r_1 \chi_p(\mathbf{r}_2)\chi_r(\mathbf{r}_2) \frac{1}{|\mathbf{r}_2 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1)\chi_s(\mathbf{r}_2) \tag{77}$$

$$S_{pq} = \langle \chi_p | \chi_q \rangle \tag{78}$$

Unfortunately, thsi is not a generalized eigenvalue equation because of the presence of the variables C_r and C_s inside the brackets on the left hand side. However, we can carry out a self-consistency iteration process as described earlier. By keeping C_r and C_s fixed, we solve the equationo for the C_q's. We then replace the coefficients by the new solutiono, and iterate until convergence is achieved.

In order to calculate the matrix elements, we shall use Gaussian $l = 0$ basis functions, just as in the case of the hydrogen atom:

$$\chi_p(\mathbf{r}) = e^{-\alpha_p r^2}. \tag{79}$$

We shall take the optimal values of α_p found by solving the non-linear problem:

$$\alpha_1 = 0.298073 \tag{80}$$
$$\alpha_2 = 1.242567 \tag{81}$$
$$\alpha_3 = 5.782948 \tag{82}$$
$$\alpha_4 = 38.474970. \tag{83}$$

The matrix elements for the kinetic and Coulomb terms are similar to those calculated for the hydrogen atom, except for an extra factor of Z in the nuclear attraction. The matrix elements ofr Q_{pqrs} are

$$Q_{pqrs} = \frac{2\pi^{5/2}}{(\alpha_p + \alpha_q)(\alpha_r + \alpha_s)\sqrt{\alpha_p + \alpha_q + \alpha_r + \alpha_s}}. \tag{84}$$

The program is consructed as follows:
- First, the $N \times N$ matrices h_{pq}, S_{pq} and the $N \times N \times N \times N$ tensor Q_{pqrs} are calculated.
- Initial values for the C_p coefficients are chosen (all equal, for instance).
- These values are used to contruct the F_{pq} matrix given by

$$F_{pq} = h_{pq} + \sum_{rs} C_r C_s Q_{pqrs}. \tag{85}$$

- We solve the generalized eigenvalue problem. For the ground-state, we keep only the eigenvector with the lowest eigenvalue.
- We calculate the ground-state energy as:

$$E = 2\sum_{pq} C_p C_q h_{pq} + \sum_{pqrs} Q_{pqrs} C_p C_q C_r C_s. \tag{86}$$

- The new solution of the geenralized eigenvalue problem is then used to contruct the new matrix F_{pq} and we repeat until the energy converges.

Exercise 3.1: Helium atom

Wirte a program to calculate the ground-state energy of the helium atom. If your program is correct, your result shoul dbe $E = -2.85516038$.

3.4 Many electron systems and the Slater determinant

3.4.1 Two-particle case

In the helium problem, we could make use of the fact that in the ground-state, the antisymmetry is taken care of by the spin part of the wave-function, whcih in turn drops out of the Schrödinger equation. If we are after excited states, or if more than two electrons are involved, the antisymmetry requirement affects the orbital part of the wave-function and must be taken into account.

Let us take another look at the two-particle case. The simplest way to approximate the wave function of a many-particle system is to take the product of properly chosen wave functions of the individual particles. For the two-particle case, we have

$$\Psi(\mathbf{x_1}, \mathbf{x_2}) = \psi_{\mathbf{1}}(\mathbf{x_1})\psi_{\mathbf{2}}(\mathbf{x_2}). \tag{87}$$

This expression is used in the Hartree method as an ansatz for the many-particle wave function and is known as a Hartree product. However, it is not satisfactory for fermions, such as electrons, because the wave function is not antisymmetric. An antisymmetric wave function can be mathematically described as follows:

$$\Psi(\mathbf{x_1}, \mathbf{x_2}) = -\boldsymbol{\Psi}(\mathbf{x_2}, \mathbf{x_1}). \tag{88}$$

Therefore the Hartree product does not satisfy the Pauli principle. This problem can be overcome by taking a linear combination of both Hartree products

$$\Psi(\mathbf{x_1}, \mathbf{x_2}) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}}}\{\psi_{\mathbf{1}}(\mathbf{x_1})\psi_{\mathbf{2}}(\mathbf{x_2}) - \psi_{\mathbf{1}}(\mathbf{x_2})\psi_{\mathbf{2}}(\mathbf{x_1})\} = \frac{\mathbf{1}}{\sqrt{\mathbf{2}}}\begin{vmatrix} \psi_1(\mathbf{x_1}) & \psi_2(\mathbf{x_1}) \\ \psi_1(\mathbf{x_2}) & \psi_2(\mathbf{x_2}) \end{vmatrix} \tag{89}$$

where the coefficient is the normalization factor. This wave function is antisymmetric and no longer distinguishes between fermions. Moreover, it also goes to zero if any two wave functions or two fermions are the same. This is equivalent to satisfying the Pauli exclusion principle.

If we now take into account the spin degree of freedom $\psi(\mathbf{x}) = \phi(\mathbf{r})|\sigma\rangle$, we obtain:

$$\Psi(\mathbf{x_1}, \mathbf{x_2}) = \frac{\mathbf{1}}{\sqrt{\mathbf{2}}}\{\phi_{\mathbf{1}}(\mathbf{r_1})|\sigma_{\mathbf{1}}\rangle_{\mathbf{1}}\phi_{\mathbf{2}}(\mathbf{r_2})|\sigma_{\mathbf{2}}\rangle_{\mathbf{2}} - \phi_{\mathbf{1}}(\mathbf{r_2})|\sigma_{\mathbf{2}}\rangle_{\mathbf{1}}\phi_{\mathbf{2}}(\mathbf{r_1})|\sigma_{\mathbf{1}}\rangle_{\mathbf{2}}\} \tag{90}$$

3.4.2 General case: the many body wave-function

When considering a many-electron system, we must remember that the electrons are identical particles. This is seen in the Hamiltonian, exchanging indices i and j does not change the Hamiltonian. We say that the Hamiltonian commutes with the particle exchange operator P_{ij}. This operator has the effect of exchanging the coordinates of particles I and j:

$$P_{ij}\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_i, \cdots, \mathbf{x}_j, \cdots, \mathbf{x}_N) = \Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_j, \cdots, \mathbf{x}_i, \cdots, \mathbf{x}_N), \tag{91}$$

where the coordinates $\mathbf{x}_i$ contain the orbital and spin part.

Since the Hamiltonian commutes with the operator P_{ij}, its eigenvectors should simultaneously be eigenvectors of P. Since $P^2 = 1$, its eigenvalues are either $+1$ or -1. In the first case, we say that the particles are bosons, while in the second case, we call them fermions. Since electrons are fermions, we find that their many-body wave-function whould be antisymmetric under exchanges.

Let us forget about antisymmetry for a moment. For the case of an independent particle Hamiltonian, which is the sum of one-electron Hamiltonians, we can write the solution to the Schrödinger equation as a product of one-particle wave-functions:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) = \psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)\cdots\psi_N(\mathbf{x}_N). \tag{92}$$

the one-particle states are eigenstates of the one-particle Hamiltonians. The probability density id then given by

$$\rho(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_N) = |\psi_1(\mathbf{x}_1)|^2|\psi_2(\mathbf{x}_2)|^2|...|\psi_N(\mathbf{x}_N)|^2, \tag{93}$$

which is just the product of one-particle densities. Such a probability density is called *uncorrelated.*

Of course, a state with the coordinates permuted is also a solution, as are linear combinations of such states. But the requirement of antisymmetry implies that the wave function should have the form:

$$\Psi_{AS} = \frac{1}{N!}\sum_{\mathbf{P}} \mathrm{sgn}_P \mathbf{P}\psi_1(\mathbf{x}_1)\psi_2(\mathbf{x}_2)...\psi_N(\mathbf{x}_N). \tag{94}$$

P is a permutation operator that permutes the coordinates, and not the wave-functions. The sign in the sum can be $+1$ or -1 according to wether the permutation can be written as a product of even or odd pair interchanges, respectively.

We can write this wave-function as a Slater determinant:

$$\Psi_{AS} = \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix} \quad ,$$

Its is important to note that after the antisymmetrization procedure the electrons are correlated. To see this we write the prbability density of finding two electrons with coordinates $\mathbf{x}_1$ and $\mathbf{x}_2$:

$$\begin{aligned} \rho(\mathbf{x}_1, \mathbf{x}_2) &= \int dx_3 \cdots dx_N |\Psi_{AS}|^2 && (95) \\ &= \frac{1}{N(N-1)} \sum_{k,l} \left[|\psi_k(\mathbf{x}_1)|^2 |\psi_l(\mathbf{x}_2)|^2 - \psi_k^*(\mathbf{x}_1)\psi_k(\mathbf{x}_2)\psi_l^*(\mathbf{x}_2)\psi_l(\mathbf{x}_1) \right] && (96) \end{aligned}$$

To find the probability of having two electrons at positions $\mathbf{r}_2$ and $\mathbf{r}_2$ we have to sum over the spin variables:

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \sum_{s_1, s_2} \rho(\mathbf{x}_1, \mathbf{x}_2). \tag{97}$$

We can see that for ψ_k and ψ_l having opposite spin, the second term in (96) vanishes and therefore opposite spin oribitals are uncorrelated, but for equal spins, the two terms cancel when $\mathbf{r}_1 = \mathbf{r}_2$, so electrons with equal spins cannot sit on the same point in space and are kept apart. Every electron is found surrounded by an exchange hole in which other electrons having similar spin are hardly found. This is nothing else but a manifestation of Pauli's exclussion principle.

3.5 Hartree-Fock theory

3.5.1 The Hartree-Fock equations

The full Hartree-Fock equations are given by

$$H_{HF}\psi_k = \epsilon_k \psi_k, \tag{98}$$

with

$$H_{HF}\psi_k = \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R_n}|}\right]\psi_k(\mathbf{x}) + \sum_{l=1}^{N}\int dx'|\psi_l(\mathbf{x}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x}) \tag{99}$$

$$-\sum_{l=1}^{N}\int dx'\psi_l^*(\mathbf{x}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x}')\psi_l(\mathbf{x}) \tag{100}$$

Notice that the wavefunctions deppend on the generalize coordinate $\mathbf{x}$, which includes the orbital and spin parts. The right hand side of the equations consists of four terms. The first and second give rise are the kinetic energy contribution and the electron-ion potential. The third term, or Hartree term, is the simply electrostatic potential arising from the charge distribution of N electrons. As written, the term includes an unphysical self-interaction of electrons when $l = k$. This term is cancelled in the fourth, or exchange term. The exchange term results from our inclusion of the Pauli principle and the assumed determinantal form of the wavefunction. Notice that thsi term is non-local, its value at $\mathbf{r}$ is determined by the value assumed by ψ_k at all possible positions $\mathbf{r}'$.

We can rewrite H_{HF} as the sum of different terms:

$$H_{HF} = h + J - K, \tag{101}$$

with

$$h = \sum_i \left[-\frac{1}{2}\nabla_i^2 - \sum_n \frac{Z_n}{|\mathbf{r_i}-\mathbf{R_n}|}\right] \tag{102}$$

$$J(\mathbf{x})\psi_k(\mathbf{x}) = \sum_{l=1}^{N}\int dx'|\psi_l(\mathbf{x}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_k(\mathbf{x}) \tag{103}$$

$$K(\mathbf{x})\psi_k(\mathbf{x}) = \sum_{l=1}^{N}\int dx'\psi_l^*(\mathbf{x}')\psi_k(\mathbf{x}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\psi_l(\mathbf{x}). \tag{104}$$

We can eliminate the sum over the spin indices by summing over them, to find the operators acting on the orbital part, only. The h operators remains the same since it does not contain any spin dependence. The new operators J and K acting on the orbital parts then read:

$$J(\mathbf{r})\phi_k(\mathbf{r}) = 2\sum_{l=1}^{N}\int d^3r'|\phi_l(\mathbf{r}')|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_k(\mathbf{r}) \tag{105}$$

$$K(\mathbf{r})\phi_k(\mathbf{r}) \;=\; \sum_{l=1}^{N} \int d^3r' \phi_l^*(\mathbf{r}')\phi_k(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_l(\mathbf{r}). \tag{106}$$

Multiplying by $\phi_k^*(\mathbf{r})$ and integrating over $\mathbf{r}$ we obtain the expression for the energy:

$$E = 2\sum_k \langle \phi_k|h|\phi_k\rangle + \sum_k \langle \phi_k|2J-K|\phi_k\rangle \tag{107}$$

where the factors 2 arise from the sum over the spin indices.

3.5.2 Koopman's theorem

If we assume that the spectrum does not change when we excite an electron above the ground-state, we can prove that the energy required to add the electron to an excited state, is precisely ϵ_k, the eigenvalues of H_{HF}. In order to do that we need to calculate $E_{N+1}^k - E_N$, where we have added an electron in the orbital k. The energy can be easily computed to yield:

$$E_{N+1}^k - E_N = \langle \phi_k|h|\phi_k\rangle + \langle \phi_k|2J-K|\phi_k\rangle = \epsilon_k. \tag{108}$$

If one sums over all occupied states, the two-body term will become twice larger than 107. Thus, the total energy is also given by:

$$E = \sum_k \left[\epsilon_k - \frac{1}{2}\langle k|2J-K|k\rangle\right], \tag{109}$$

which is obviously not the same as the sum over all the eigenvalues.

3.6 Matrix form of the Hartree-Fock equations

Same as in previous chapters, we are going to expand the wavefunctions as linear combinations of a finite number of basis states:

$$\phi_k(\mathbf{r}) = \sum_p C_{pk}\chi_p(\mathbf{r}). \tag{110}$$

For a given basis, we obtain the following matrix equation, which is known as *Roothaan equation*:

$$FC_k = \epsilon S C_k, \tag{111}$$

where S is the overlap matrix for the orbital basis, and the matrix F is given by:

$$F_{pq} = h_{pq} + \sum_k \sum_{pq} C^*_{rk} C_{sk} (2\langle ps|g|qs\rangle - \langle pr|g|sq\rangle) \tag{112}$$

where

$$h_{pq} = \langle p|h|q\rangle = \int d^3r \chi^*_p(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r} - \mathbf{R}_n|} \right] \chi_q(\mathbf{r}), \tag{113}$$

and

$$\langle pr|g|qs\rangle = \int d^3r_1 d^3r_2 \chi^*_p(\mathbf{r}_1) \chi^*_r(\mathbf{r}_2) \frac{1}{|\mathbf{r}_2 - \mathbf{r}_2|} \chi_q(\mathbf{r}_1) \chi_s(\mathbf{r}_2). \tag{114}$$

As we have seen before, these equations should be solved by a self-consistent iterative procedure.

It is convenient to introduce the density matrix, defined as

$$\rho_{pq} = 2\sum_k C_{pk} C^*_{qk} \tag{115}$$

which is the matrix representation for the operator

$$\rho = 2\sum_k |\phi_k\rangle\langle\phi_k|. \tag{116}$$

Using this expression we can rewrite the Fock matrix as:

$$F_{pq} = h_{pq} + \frac{1}{2}\sum_{rs} \rho_{rs} (2\langle ps|g|qs\rangle - \langle pr|g|sq\rangle), \tag{117}$$

and the energy is given by:

$$E = \sum_{pq} \rho_{pq} h_{pq} + \frac{1}{2}\sum_{pqrs} \rho_{pq}\rho_{rs} \left[\langle pr|g|qs\rangle - \frac{1}{2}\langle pr|g|sq\rangle \right]. \tag{118}$$

4 Density Functional Theory

4.1 Introduction

We are interested in calculating the ground state energy of a generic Hamiltonian for a system of many electons interacting with an external potential $V_{ext}(\mathbf{r})$. We assume this external potential depends only on the coordinates $\mathbf{r}$, and it is generaly given by the interaction with the nuclei, as we have seen in previous sections. Therefore the Hamiltonian reads: For a many-body system, the Hamiltonian is given by

$$\begin{aligned} H &= \sum_i \left[\frac{1}{2}\nabla_i^2 + V_{ext}(\mathbf{r}_i)\right] + \sum_{i,j>i} \frac{1}{|\mathbf{r}-\mathbf{r}_j|} && (119) \\ &= T + V_{ext} + V_{e-e}, && (120) \end{aligned}$$

where we have also included the electron-electron interactions. V_{ext} is an external potential, which, in systems of interest to us, is the Coulomb attraction by the nuclei.

The kinetic energy and the external potential are one-particle terms, while the electron-electron term is a two-body interaction. We can rewrite the energy as

$$E = \langle\psi|H|\psi\rangle = \int d^3r_1 d^3r_2 \cdots d^3r_N \psi^*(\mathbf{r}_1,\cdots,\mathbf{r}_N) H \psi(\mathbf{r}_1,\cdots,\mathbf{r}_N) \quad (121)$$

$$= N\int d^3r_1 d^3r_2 \cdots d^3r_N \psi^*(\mathbf{r}_1,\cdots,\mathbf{r}_N)\left[T(\mathbf{r}_1) + V_{ext}(\mathbf{r}_1)\right]\psi(\mathbf{r}_1,\cdots,\mathbf{r}_N) + \quad (122)$$

$$\frac{N(N-1)}{2}\int d^3r_1 d^3r_2 \cdots d^3r_N \psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\frac{1}{r_{12}}\psi(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N). \quad (123)$$

Let us define the density matrix as

$$g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}'_1,\mathbf{r}'_2) = \int d^3r_3 d^3r_4 \cdots d^3r_N \psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_N)\psi(\mathbf{r}'_1,\mathbf{r}'_2,\cdots,\mathbf{r}_N) \quad (124)$$

and the pair-correlation as

$$g(\mathbf{r}_1,\mathbf{r}'_1) = \int d^3r_2 d^3r_3 \cdots d^3r_N \psi^*(\mathbf{r}_1,\mathbf{r}_2,\cdots,r_N)\psi(\mathbf{r}'_1,\mathbf{r}_2,\cdots,\mathbf{r}_N). \quad (125)$$

and the density as:

$$n(r) = \int d^3r_2 d^3r_3 \cdots d^3r_N \psi^*(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N)\psi(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_N). \quad (126)$$

We can now write the interaction part of the enrgy as:

$$\langle V_{e-e}\rangle = \frac{N(N-1)}{2}\int d^3r_1 d^3r_2 g(\mathbf{r}_1,\mathbf{r}_2)\frac{1}{r_{12}}. \tag{127}$$

$$\langle V_{ext}\rangle = \int d^3r\, n(\mathbf{r})V_{ext}(\mathbf{r}) \tag{128}$$

What's noteworthy about these expression is that we do not need the wave-function to calculate this quantity, we only need the density and the pair-correlation function, which is complicated, or even impossible to evaluate.

Density Functional Theory goes a step further, and it states that we can evaluate the energy if we just know the density.

Thsi is a remarkable result, and the implications are very powerful: we know that wafe-functions are very complicated objects compared to the density. Working with the density simplifies the problem enormously. However, we notice right away that we have avoided writing the kinetic energy and the interaction energies as fcuntiosn of the density. This is because we simply do not know how to do it! Density functional theory hints at a method to get good guesses by using the so-called Kohn-Sham equations, and the local density approximation, and this is what we are going to leanr in the course of this section.

4.1.1 Some considerations about exchange

The pair correlation function satisfies a very important sum-rule:

$$n(\mathbf{r})\int d^3r'\,(g(\mathbf{r},\mathbf{r}')-1) = -1, \tag{129}$$

valid for all positions $\mathbf{r}$ and totally independent of the interactionos and the Hamiltonian.

The effect of the pair correlation is to keep the particles appart by virtue of the interaction and Pauli's exclusion principle. Of these, we expect the interaction to give the larger contribution. In fact, setting $g = 1$ amounts to the Hartree potential, whcih neglects all effects of exchange and correlation, but still takes Coulomb repulsion into account. Furthermore, we expect that at large distances the particles interact very weakly, thus $g(\mathbf{r},\mathbf{r}') \to 1$ as $|\mathbf{r}-\mathbf{r}'| \to \infty$. These observations lead us to separating V_{e-e} into two contrubutions by rewriting $g = 1 + (g-1)$, whcih will give us one pure interaction term –or Hartree term — from the first 1 and one, hopefully small exchange correlation term from the $(g-1)$:

$$\begin{aligned} V_{e-e} &= \frac{1}{2}\int d^3r_1\, d^3r_2\, n(\mathbf{r}_1)n(\mathbf{r}_2)\frac{1}{r_{12}} \qquad (130)\\ &+ \frac{1}{2}\int d^3r_1\, d^3r_2\, n(\mathbf{r}_1)n(\mathbf{r}_2)\frac{1}{r_{12}}\left(g(\mathbf{r}_1,\mathbf{r}_2)-1\right). \qquad (131)\end{aligned}$$

At this point it is appropriate to say a few words about the Hartree-Fock approximation, in which exchange is taken into account by requiring all wavefunctions to be Slater determinants. It still ignores the correlation energy, whcih can be defined as exactly that: everything that is ignored in Hartree-Fock.

4.2 Functionals and functional derivatives

Functionals are mappings from function spaces to real or complex numbers. A general representation for a function F is

$$\begin{aligned} F[g] &= F_0 + \int dx F_1(x)g(x) \qquad (132)\\ &+ \int dx_1 \int dx_2 F_2(x_1,x_2)g(x_1)g(x_2) \qquad (133)\\ &+ \int dx_1 \int dx_2 \int dx_3 F_3(x_2,x_2,x_3)g(x_1)g(x_2)g(x_3) + \cdots \qquad (134)\end{aligned}$$

where the kernels F_i are general functions.

Now let $g \to g + \Delta g$. To linear order in Δg we obtain

$$\begin{aligned} F[g+\Delta g] &= F[g] + \int dx F_1(x)\Delta g(x) \qquad (135)\\ &+ 2\int dx_1 \int dx F_2(x_1,x)g(x_1)\Delta g(x) \qquad (136)\\ &+ 3\int dx_1 \int dx_2 \int dx F_3(x_1,x_2,x)g(x_1)g(x_2)\Delta g(x) + \cdots \qquad (137)\end{aligned}$$

where we have assumed that the functions F_i are symmetric functions of their arguments.

We can rewrite this equation as

$$F[g+\Delta g] = f[g] + \int dx \frac{\delta F[g]}{\delta g(x)}\Delta g(x) \qquad (138)$$

where

$$\frac{\delta F[g]}{\delta g(x)} = F_1(x) + 2\int dx_1 F_2(x_1, x) g(x_1) \tag{139}$$

$$+ \ 3\int dx_1 \int dx_2 F_3(x_1, x_2, x) g(x_1) g(x_2) + \cdots \tag{140}$$

In analogy, we find

$$\frac{\delta^2 F[g]}{\delta g(x)\delta g(x')} = 2F_2(x, x') + 3\int dx_1 F_3(x_1, x, x') g(x_1) + \cdots \tag{141}$$

4.3 The Coulomb (Thomas-Fermi) functional

For the classical part of the potential, Thomas and Fermi employed the Coulomb potential energy functional

$$U[n(r)] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r d^3r' \tag{142}$$

Again, $U[n]$ depends only on the charge density n and does not depend on its gradient, Laplacian, or other higher-order derivatives. Therefore,

$$U_0 = 0; \ \ U_1 = 0; \ \ U_2(\mathbf{r}, \mathbf{r}') = \frac{1}{2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}; \ \ U_{n>2} = 0; \tag{143}$$

and we find

$$\frac{\delta U[n]}{\delta n} = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' \tag{144}$$

The second functional derivative of the Coulomb potential energy functional is

$$\frac{\delta^2 U[n]}{\delta n^2} = \frac{1}{|\mathbf{r}-\mathbf{r}'|} \tag{145}$$

We should make the following observation. Thsi potential contains a self-interaction between a particle and itself, which is unphysical. It does not take into account the Pauli principle, and therefore, this functional should be corrected to cancel the effects of the self-interaction and take exchange into account properly. Notice that this is equivalent to the Hartree potential in the Hartree-Fock approximation.

4.4 Hohenberg-Kohn theorems

4.4.1 H-K theorem I

The Hohenberg-Kohn theorem[11] states that if N interacting electrons move in an external potential $V_{ext}(\mathbf{r})$, the ground-state energy is a unique functional of the density $n(\mathbf{r})$.

Thus the ground state electron density is sufficient to construct the full Hamilton operator and hence to calculate - in principle - any ground state property of the system without the knowledge of the many electron wavefunction. Alternatively formulated, this means that any ground state property can be expressed in terms of the ground state electron density $n(\mathbf{r})$.

4.4.2 H-K theorem II

The groundstate energy can be obtained variationally: the density that minimises the total energy is the exact groundstate density.

Although the Hohenberg-Kohn theorems are extremely powerful, they do not offer a way of computing the ground-state density of a system in practice. About one year after the seminal DFT paper by Hohenberg and Kohn, Kohn and Sham devised a simple method for carrying-out DFT calculations, that retains the exact nature of DFT. This method is described next.

4.5 DFT formalism and derivation of the Kohn-Sham equations

We define the energy as a functional of the density as

$$E[n(\mathbf{r})] = \min_{\Psi|n} \langle \Psi | H | \Psi \rangle \tag{146}$$

where we are minimizing with respect to all the possible wavefunctions compatible with the density $n(\mathbf{r})$.

The ground-state can be found by minimizing the functional with respect to the density, subject to the constraint:

$$\int d^3 r n(\mathbf{r}) = N \tag{147}$$

where N is the total number of electrons.

4.5.1 Non-interacting case

Consider the separation of the Hamiltonian as

$$H = H_0 + V_{ext} \tag{148}$$

where H_0 corresponds to the non-interacting homogeneouos electron gas.

Then the functional reads:

$$E[n] = F[n] + \int d^3rn(\mathbf{r})\, V_{\text{ext}}(\mathbf{r}) \tag{149}$$

with

$$F[n] = \min_{\Psi|n} \langle \Psi | H_0 | \Psi \rangle \tag{150}$$

The problem of treating the many-body problem lies in the electron-electron interation. In the non-interacting case, $E[n]$ has a kinetic contribution and a contribution from the external potential V_{ext}:

$$E[n] = T[n] + \int d^3rn(\mathbf{r})\, V_{\text{ext}}(\mathbf{r}) \tag{151}$$

The variation of E with respect to the density leads to the following equation:

$$\frac{\delta T[n]}{\delta n(\mathbf{r})} + V_{ext}(\mathbf{r}) = \mu, \tag{152}$$

where μ is the chemical potential and acts as a Lagrange multiplier associated to the density contraint. The problem with this expression is that we still don not know how to write tthe kinetic energy as a function of the density. Fortunately, we know how to solve the non-interacting case, and the exact ground-state has the form of a Slater determinant. The correspoding Schrödinger equation reads:

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) \right] \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}). \tag{153}$$

The ground-state density of given by

$$n(\mathbf{r}) = \sum_{k=1}^{N} |\psi_k(\mathbf{r})|^2, \tag{154}$$

and this solution is self-consistent.

From the exact solution of the non-interacting case, we know that $T[n]$ is independent of the external potential V_{ext}.

4.5.2 Interacting system

The energy-functional for a many-body system with the electronic interaction taken into account reads

$$E\,[n(\mathbf{r})] = T\,[n(\mathbf{r})] + \int d^3 r n(\mathbf{r})\, V_{\text{ext}}(\mathbf{r}) + \frac{1}{2}\int d^3 r d^3 r' n(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}) + E_{xc}[n], \tag{155}$$

where the last term, the exchange correlation energy, contains by definition all the contributions not taken into account by the first three terms. We have made no approximation, we simply moved all the unknown correlations into E_{xc}, whcih depends on the density instead of the explicit form of the wavefunction. Varying this equation with respet to the density we obtain:

$$\frac{\delta T[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + \int d^3 r' n(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|} + V_{ext}(\mathbf{r}) = \mu, \tag{156}$$

This equation has the same form as (152) with the difference that the potential has been replaced by an effective one:

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + \int d^3 r' n(\mathbf{r}') \frac{1}{|\mathbf{r}-\mathbf{r}'|}. \tag{157}$$

The corresponding Schrödinger equation for the one-particle wavefunctions is

$$\left[-\frac{1}{2}\nabla^2 + V_{eff}(\mathbf{r})\right]\psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}). \tag{158}$$

Same as for Hartree-Fock, summing over all the eigenvalues leads to overestimating the Hartree energy by a factor of 2, and further difference in the exchange correlation energy. The corresponding expression for the ground-state energy is:

$$E = \sum_{k=1}^{N} \epsilon_k - \frac{1}{2}\int d^3 r d^3 r' n(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} n(\mathbf{r}') + E_{xc}[n] - \int d^3 r V_{xc}[n(\mathbf{r})] n(\mathbf{r}). \tag{159}$$

where

$$V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \tag{160}$$

These are the so-called Kohn and Sham equations.

From here we obtain the kinetic term as:

$$T[n] = \sum_{i=1}^{N} \epsilon_i - \int n(\mathbf{r}) V_{eff}(\mathbf{r}) d^3r \tag{161}$$

and the density

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2. \tag{162}$$

It is very important to be careful when considering the individual eigenvalues ϵ_i. In general they cannot be associated to any excitation energy, which would be a nive and natural interpretation.

The main problem with the Kohn-Sham equations is that we do not know the exact expression for the exchange functional, we can only use some properly chosen functionals based on educated guesses, as we are going to see next.

4.6 The local density approximation - LDA

In the local density approximation (LDA), the value of $E_{xc}[n(\mathbf{r})]$ is approximated by the exchange-correlation energy of an electron in an homogeneous electron gas of the same density $n(\mathbf{r})$, i.e.

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}(n(\mathbf{r})) n(\mathbf{r}) d\mathbf{r} \quad .$$

The most accurate data for $\epsilon_{xc}(n(\mathbf{r}))$ is from Quantum Monte Carlo calculations. The LDA is often surprisingly accurate and for systems with slowly varying charge densities generally gives very good results. The failings of the LDA are now well established: it has a tendency to favour more homogeneous systems and over-binds molecules and solids. In weakly bonded systems these errors are exaggerated and bond lengths are too short. In good systems where the LDA works well, often those mostly consisting of *sp* bonds, geometries are good and bond lengths and angles are accurate to within a few percent. Quantities such as the dielectric and piezoelectric constant are approximately 10% too large.

The principle advantage of LDA-DFT over methods such as Hartree-Fock is that where the LDA works well (correlation effects are well accounted for) many experimentally relevant physical properties can be determined to a useful level of accuracy. Difficulties arise where it is not clear whether the LDA is applicable. For example, although the LDA performs well in bulk group-IV semiconductors it is not immediately clear how well it performs at surfaces of these materials.

4.6.1 Limitations

Despite the remarkable success of the LDA, its limitations mean that care must be taken in its application. For systems where the density varies slowly, the LDA tends to perform well, and chemical trends are well reproduced. In strongly correlated systems where an independent particle picture breaks down, the LDA is very inaccurate. The transition metal oxides XO (X=Fe,Mn,Ni) are all Mott insulators, but the LDA predicts that they are either semiconductors or metals. The LDA has been applied to high T_c superconductors, but finds several to be metallic, when in reality they are insulating at 0K.

The LDA finds the wrong ground state for in many simpler cases. For example, the LDA finds the wrong ground state for the titanium atom. The LDA does not account for van der Waals bonding, and gives a very poor description of hydrogen bonding. These phenomena are essential for most of biochemistry: the structure of DNA of depends critically on hydrogen bonding, as do the changes in the structure of most molecules on solvation.

The success of the LDA has been shown by QMC calculations to result from a real-space cancellation of errors in the LDA exchange and correlation energies. The cancellation represents a difficulty when improvements to the LDA are attempted, as an improvement in only the exchange or correlation contributions may give worse results.

An obvious approach to improving the LDA is to include gradient corrections, by making E_{xc} a functional of the density and its gradient:

$$E_{xc}[n(\mathbf{r})] = \int d^3r \epsilon_{xc}(n(\mathbf{r}))n(\mathbf{r}) + \int d^3r F_{xc}[n(\mathbf{r}), |\nabla n(\mathbf{r})|] d\mathbf{r} \quad ,$$

where F_{xc} is a correction chosen to satisfy one or several known limits for E_{xc}.

Clearly, there is no unique recipe for F_{xc}, and several dozen functionals have been proposed in the literature. They do not always represent a systematic improvement over the LDA and results must be carefully compared against experiment.The development of improved functionals is currently a very active area of research and although incremental improvements are likely, it is far from clear whether the research will be successful in providing the substantial increase in accuracy desired.

4.7 More about exchange

Let us define a new quantity

$$n_{xc}(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}')(g(\mathbf{r}, \mathbf{r}') - 1). \tag{163}$$

We can easily see that the exchange correlation energy may be written

$$E_{xc}[n] = \frac{1}{2} \int d^3r_1\, d^3r_2\, n(\mathbf{r}_1) n_{xc}(\mathbf{r}_1, \mathbf{r}_2) \frac{1}{r_{12}}. \tag{164}$$

This is the Coulomb interaction of each electron with a charge distribution n_{xc}, whcih can be interpreted as a conditional density. This conditional density vanished as the distance between the particles goes to zero, and may be interpreted as a "hole" surrounding each particle, and it is named *exchange correlation hole*. We can see that this hole orrespond to a unit of charge by anotehr sum-rule:

$$\int d^3r\, n_{xc}(\mathbf{r}, \mathbf{r}') = -1. \tag{165}$$

We can consider $-n_{xc}$ as a normalizationo factor and define the radius of the exchange hole as:

$$\left\langle \frac{1}{R} \right\rangle = -\int d^3r \frac{n_{xc}(\mathbf{r}, \mathbf{R})}{|R|}. \tag{166}$$

Thsi leads to

$$E_{xc}[n] = -\frac{1}{2} \int d^3r\, n(\mathbf{r}) \left\langle \frac{1}{R} \right\rangle \tag{167}$$

showing that, privided that the sum-rule is satisfied, the exchange-correlation energy depends only weakly on the details of n_{xc}. Thsi means that even if our approximation is nto able to describe the detailed spatial shape of the hole, as long as the sum-rule is fulfuilled, the errors are small, and LDA will produce good results.

4.8 Solution to the Kohn-Sham equations

We can solve the Kohn-Sham equations self-consistently, in the same spirit as we solved the Hartree-Fock equations in the previous section. The first step is to pick a suitable exchange functional.

1. Choose and appropriate atomic basis χ_p
2. We write the variational ansatz as:
$$\psi_k = \sum_p C_{kp}\chi_p \tag{168}$$
3. We compute the density as:
$$n(\mathbf{r}) = \sum_k |\psi_k(\mathbf{r})|^2 \tag{169}$$
4. We replace the density in the Kohn-Sham equations to find the new eigenfunctions and eigenvalues. Thsi means funding the coefficients C_{kp}.
5. Go to 3 to compute the new density and iterate until convergence is achieved.

4.9 Pros and Cons of the DFT

- It is computationally very “cheap”.
- Stablished exchanged functinals are “good”.
- There is no systematic way to imporve the functionals.
- Dispersion of electrons in not included in the functionals.
- Exchange functionals do not cancel the self-interaction properly.
- If one plugged the density for an excited state, would the same functional give the right energy?

5 Methods for band-structure calculations

5.1 The tight-binding approximation

It is instructive to look at the simple example of a chain composed of hydrogen-like atoms with a single s-orbital. This will serve to illustrate the main concepts in band structure calculations, such as momentum space, and Bloch functions.

Let us first define some identities: The wave function of an isolated atomic orbital centered on atom j is $\phi(\mathbf{r}-\mathbf{R}_j)$. We are going to use Direc's notation from now one, meaning that:

$$\phi(\mathbf{r}-\mathbf{R}_j) \equiv \langle \mathbf{r}|j\rangle, \tag{170}$$

$$\int d^3r \phi^*(\mathbf{r}-\mathbf{R}_j)\phi(\mathbf{r}-\mathbf{R}_i) \equiv \langle i|j\rangle \tag{171}$$

We propose a solution of the form:

$$|\psi\rangle = \sum_{i=0}^{N-1} c_i|i\rangle \tag{172}$$

We are going to make the following assumptions:

$$\begin{aligned} \langle i|j\rangle &= \delta_{i,j} && (173)\\ \langle i|H|j\rangle &= -t\delta_{j,i\pm1} && (174)\\ \langle i|H|i\rangle &= \epsilon. && (175) \end{aligned}$$

The first one implies orthogonality of orbitals sitting on different sites, and this implies, as we are going to see later, that these are "Wannier orbitals".The second line means that the Hamiltonian only mizes orbitals sitting on neighboring sites, while the third just defines a "site energy", which is just a constant shift. We are also neglectning the electron-electron interaction.

As a consequence of the above, the Hamiltonian matrix will be band diagonal:

$$H = \begin{pmatrix} \epsilon & -t & 0 & 0 & & \cdots & 0 \\ -t & \epsilon & -t & 0 & & \cdots & 0 \\ 0 & -t & \epsilon & -t & & \cdots & 0 \\ 0 & 0 & -t & \epsilon & -t & \cdots & 0 \\ \vdots & & & & & & \vdots \\ 0 & \cdots & & & & \epsilon & -t \\ 0 & \cdots & & & & -t & \epsilon \end{pmatrix} \tag{176}$$

Here we assumed periodic boundary conditions, meaning:

$$\langle 0|H|N-1\rangle = -t \tag{177}$$

$$\langle N-1|H|0\rangle = -t \tag{178}$$

and obviously, the Hamiltonian is real and symmetric.

We find the solution by writing the wavefunction as a plane wave:

$$c_i = \frac{1}{\sqrt{N}} e^{ikR_i} \tag{179}$$

Because of the periodic boundary conditions, we have to impose a condition over the allowed values of k:

$$e^{ikNa} = 1 \Rightarrow k = \frac{2\pi}{Na} m \ \ ; \text{m : integer} \tag{180}$$

The resulting wavefunction is:

$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{i=0}^{N-1} e^{ikR_i} |i\rangle. \tag{181}$$

It is easy to verify by calculating $H|\psi_k\rangle$, that it is indeed an eigenstate with an energy

$$\epsilon(k) = \epsilon - 2t \cos{(ka)} \tag{182}$$

Next, we are going to verify that it also is an eigenstate of the displacement operator T_R, *i.e* that is invariant under translations of the lattice: First, we rewrite the wavefunction as:

$$|\psi_k\rangle = \frac{1}{\sqrt{N}} \sum_{i=0}^{N-1} e^{ikR_i} T_{-R_i} |0\rangle. \tag{183}$$

Then, it is easy to see that

$$\begin{aligned} T_{R_j}|\psi_k\rangle &= \frac{1}{\sqrt{N}}\sum_{i=0}^{N-1} e^{ikR_i}T_{-R_i+R_j}|0\rangle. & (184)\\ &= \frac{1}{\sqrt{N}}e^{ikR_j}\sum_{i=0}^{N-1} e^{ik(R_i-R_j)}T_{-R_i+R_j}|0\rangle. & (185)\\ &= e^{ikR_j}|\psi_k\rangle. & (186)\end{aligned}$$

Hence, our wavefunction is a Bloch state. Another thing we notice is that the energy band is periodic, with perdio $2\pi/a$. Its is customary to represent it in a region between $-\pi/a$ and $+\pi/a$, which is nothing else, but the 1D Brillouin zone.

5.2 General case: Linear Combination of Atomic Orbitals

Let us consider a more general case, independently of the form of the Hamiltonian and the crystal structure. We are assuming for simplicity that we have one atom per unit cell (we shall see the generalization later), and the electron-electron interarctions are ignored.

We shall write the wave function for a single site, as a linear combinatioj of atomic orbitals

$$|i\rangle = \sum_p c_p|ip\rangle, \tag{187}$$

wheer the coefficient c_i are unknown. We are also assuming that the different orbitals form a *locally* orthogonal basis:

$$\langle ip|iq\rangle = \delta_{pq}. \tag{188}$$

This does not mean that the orbitals on different sites will not have a finite overlap. Let us write a k-state as:

$$|k\rangle = \frac{1}{\sqrt{N}}\sum_{i=0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}|i\rangle. \tag{189}$$

We want to explicitly obtain a form for the eigenvalue equation

$$H|k\rangle = \epsilon(k)|k\rangle. \tag{190}$$

Applying the Hamiltonian on the state $|k\rangle$ yields:

$$H|k\rangle = \frac{1}{\sqrt{N}}\sum_{i=0,p}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i} c_p H|ip\rangle. \tag{191}$$

We now multiply from the left by $|0q\rangle$, to obtain

$$\begin{aligned}\langle 0q|H|k\rangle &= \frac{1}{\sqrt{N}}\sum_{i=0,p}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i} c_p \langle 0q|H|ip\rangle & (192)\\ &= \epsilon(k)\sum_{i=0,p}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i} c_p \langle 0q|ip\rangle. & (193)\end{aligned}$$

This leads to a generalized eigenvalue equation of the form

$$HC(k) = \epsilon(k)SC(k) \tag{194}$$

in order to calculate the matrix elements explicitly, let us break H into a pice containing the atomic potential on site 0, H_{at}, and the remaning part in a term that we call ΔU. Therefore, we obtain:

$$\begin{aligned}\langle 0p|H|0q\rangle &= \langle 0p|H_{at}|0q\rangle = \epsilon_p\delta_{pq} & (195)\\ \langle 0p|H|0q\rangle &= \langle 0p|\Delta U|iq\rangle = \gamma_{pq}(\mathbf{R}_i) & (196)\\ \langle 0p|iq\rangle &= \alpha_{pq}(\mathbf{R}_i) & (197)\end{aligned}$$

this yields

$$\begin{aligned}H_{pq} &= \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\gamma_{pq}(\mathbf{R}_i) + \epsilon_p\delta_{pq} & (198)\\ S_{pq} &= 1 + \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\alpha_{pq}(\mathbf{R}_i) & (199)\end{aligned}$$

Example 5.1: Single s band

$$H = \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\gamma(\mathbf{R}_i) + \epsilon \tag{200}$$

$$
\begin{aligned}
S &= 1 + \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\alpha(\mathbf{R}_i) && (201)\\
\epsilon(k) &= \frac{H}{S} = \frac{\epsilon + \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\gamma(\mathbf{R}_i)}{1 + \sum_{i\neq 0}^{N-1} e^{i\mathbf{k}.\mathbf{R}_i}\alpha(\mathbf{R}_i)} && (202)
\end{aligned}
$$

Going back to the linear chain, we find that the conditions we need to impose to recover the previous results are:

$$\gamma = -t \text{ for } R_i = \pm a; \;\; \alpha = 0 \tag{203}$$

An then we obtain

$$\epsilon(k) = \epsilon - 2t\cos(ka). \tag{204}$$

5.2.1 Some remarks on the tight-binding method

• The characteristic feature of the tight-binding energy bands is that hte bandwidth is determined by the small overlap integral γ. Thus, the tight-binsing bands are narrow bands, and the smaller the overlap, the narrower the bands are. In the limit of vanishing overlap, the bandwidth also vanishes and the states become N-fold degenerate. This would correspond to core electrond residing near the nucleus, resembling N isolated atoms, or atoms that are pulled very far apart.
• Interestingly, although commonly associated to the kinetic energy, the integral γ –also called hopping integral– is purely generated by the potential energy, and how it hybridizes neighboring orbitals.
• Near the bottom of the bands, the energy is quadratic in k, and the constant-energy surfaces are spherical.
• The slope of the energy curve is zero when crossing perpendicular to one of the faces of the Brillouin zone.
• In solids that are not monoatomic Bravais lattices, *i.e* they are decorated lattices with more than one atom species, the tight-binding calculation becomes more complicated. if we have more than one atom per unit cell, we can write:

$$|i\rangle = \sum_{\alpha p} c_{\alpha p}|i\alpha p\rangle \tag{205}$$

where *alpha* denotes the different atoms in the unit cell. Then, we need to generalize the equations to obtain the matrix elements $H_{\alpha p,\beta q}$, and $S_{\alpha p,\beta q}$.

5.2.2 Limitations of the tight-binding model

The main objection we can raise about the method is that we are trying to describe the wavefunction of the periodic solid as a combination of atomic orbitals that are eigenstates of a different Schrödinger equation with a differen potential and different boundary conditions. Moreover, the basis set is incomplete, since it lacks all the scattered wave eigenstates of the Schrödinger equation in the continuum. Although the wavefunction may be reasonably describe the states near the core of the atoms, it cannot pretebd to represent a Bloch state in the insterstitial region, where is must behave as a linear combination of free-electron plane waves.

The core wavefunctionos are appreciable only in de vicinity of the atom, and therefore the t-b approximation works reasonably well. However, in valence band states, that have higher energy than core states, the wavefunctions present more oscillations near the atomic cores. Moreover, they look more plane-wave-like in the intersticial regiono between atoms. For these states, the tight-binsing approximation does not work, and more sophisticated methods are required, as we will stee in the next section.

5.3 Plane Waves

From Bloch's theorem we know that

$$\phi_i(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u(\mathbf{r}) \tag{206}$$

where the function $u(\mathbf{r})$ is a periodic function with the periodicity of the lattice. This means that we can always expand it in a Fourier series as

$$u(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{K}=\mathbf{0}}^{\infty} C_{\mathbf{k}}(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}} \tag{207}$$

where $\mathbf{K}$ is a vector of the recirpocal lattice.

Let us define the PW basis as

$$\phi_{\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{K}\cdot\mathbf{r}} \tag{208}$$

We can see that this is an orthonormal basis

$$\langle \phi_{\mathbf{K}} | \phi_{\mathbf{K}'} \rangle = 0 \tag{209}$$

We can now write the wave function $\phi_{\mathbf{k}}$ in this basis as:

$$\phi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{K}=\mathbf{0}}^{\infty} C_{\mathbf{k}} \phi_{\mathbf{K}}(\mathbf{r}). \tag{210}$$

We can redefine the basis by including the phase in the exponential

$$\phi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i(\mathbf{K}+\mathbf{k})\cdot\mathbf{r}} \tag{211}$$

to obtain

$$\phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}=\mathbf{0}}^{\infty} C_{\mathbf{k}} \phi_{\mathbf{K}+\mathbf{k}}(\mathbf{r}). \tag{212}$$

5.3.1 Matrix elements

The basis is orthonormal. This implies that:

$$S^{\mathbf{k}}_{\mathbf{K},\mathbf{K}'} = \delta_{\mathbf{K},\mathbf{K}'} \tag{213}$$

$$\begin{aligned} T^{\mathbf{k}}_{\mathbf{K},\mathbf{K}'} &= -\frac{\hbar^2}{2m} \langle \phi^{\mathbf{k}}_{\mathbf{K}} | \nabla^2 | \phi^{\mathbf{k}}_{\mathbf{K}'} \rangle = \frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{K}|^2 \delta_{\mathbf{K},\mathbf{K}'} & (214) \\ V^{\mathbf{k}}_{\mathbf{K},\mathbf{K}'} &= \langle \phi^{\mathbf{k}}_{\mathbf{K}} | V | \phi^{\mathbf{k}}_{\mathbf{K}'} \rangle = \frac{1}{\Omega} \int V(\mathbf{r}) e^{i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}} d^3 r = V_{\mathbf{K}-\mathbf{K}'}. & (215) \end{aligned}$$

Hence, we obtain the following expression for the Schrödinger equation:

$$\sum_{\mathbf{K}'} \left(\frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{K}|^2 \delta_{\mathbf{K},\mathbf{K}'} + V_{\mathbf{K}-\mathbf{K}'} \right) C_{\mathbf{k}}(\mathbf{K}') = \epsilon_{\mathbf{k}} C_{\mathbf{k}}(\mathbf{K}) \tag{216}$$

A realistic calculation should include a large number of terms in the series, but usually it is necessary to impose a cutoff energy:

$$\frac{\hbar^2}{2m} |\mathbf{k}+\mathbf{K}|^2 < E_{cutoff} \Rightarrow |\mathbf{K}| < \sqrt{\frac{2mE_{cutoff}}{\hbar^2}} \tag{217}$$

5.3.2 Orthogonalized plane waves

This method is due to Herring, 1940. The idea is to build valence states using plane waves that are orthogonal to the core states. the cores states are treated as known, generally taken from tight-binding calculations using atomic orbitals.

The OPW state is constructed by orthogonalizing the wave-function with respect to the core states:

$$|\phi_{\mathbf{k}+\mathbf{K}}^{OPW}\rangle = |\mathbf{K}+\mathbf{k}\rangle - \sum_c \langle\phi_c|\mathbf{k}+\mathbf{K}\rangle|\phi_c\rangle. \tag{218}$$

where the sum runs over all core states with Bloch vector **k**.

The orthogonalized plane waves satisfy a Scrödinger equation similar to (216), but with the modified potential:

$$V_{OPW} = V + \sum_c (\epsilon - \epsilon_c)|\phi_c\rangle\langle\phi_c| \tag{219}$$

5.4 The Pseudopotential Method

The pseudopotential theory began as an extension of the OPW method. It is based on an ansatz which separates the total wave function into an oscillatory part and a smooth part, the so called pseudo wave function. The strong true potential of the ions is replaced by a weaker potential valid for the valence electrons.

Philips and Kleinman (1959) showed that one can construct a smooth valence function $\tilde{\phi}_v$ that is orthogonal to the core states ϕ_c, by using the following construction:

$$|\tilde{\phi}_v\rangle = |\phi_v\rangle + \sum_c \alpha_{cv}|\phi_c\rangle, \tag{220}$$

where the $\alpha_{cv} = \langle\phi_c|\tilde{\phi}_v\rangle$ are orthogonalization coefficients. This pseudo wavefunction satisfies the modified Schrödinger equation:

$$\left[H + \sum_c(\epsilon_v - \epsilon_c)|\phi_c\rangle\langle\phi_c|\right]|\tilde{\phi}_v\rangle = \epsilon_v|\tilde{\phi}_v\rangle. \tag{221}$$

where $H = T + V$, and V is the bare nuclear potential. This shows that it is possible to construct a pseudo-Hamiltonian

$$H_{PS} = H + \sum_c(\epsilon_v - \epsilon_c)|\phi_c\rangle\langle\phi_c| \tag{222}$$

with the same eigenvalues as the original Hamiltonian but smoother, nodeless wave function. The associated potential:

$$V_{PS} = V + \sum_c(\epsilon_v - \epsilon_c)|\phi_c\rangle\langle\phi_c| \tag{223}$$

was called a *pseudopotential.* This new correction is repulsive, and cancels the attractive potential enar the core, resulting into a smootha varying function.

To simplify the problem even further, model pseudopotentials are used in place of the actual pseudopotential, for instace:

1. Constant effective potential in the core region

$$V(r) = \begin{cases} \frac{-Z}{r}; & r > r_0 \\ \frac{-Z}{r_0}; & r \leq r_0 \end{cases} \tag{224}$$

2. Empty core model

$$V(r) = \begin{cases} \frac{-Z}{r}; & r > r_0 \\ 0; & r \leq r_0 \end{cases} \tag{225}$$

3. model potential of Heine and Abarenkov:

$$V(r) = \begin{cases} \frac{-Z}{r}; & r > r_0 \\ \text{const.}; & r \leq r_0 \end{cases} \tag{226}$$

The solution of the problem is very simple. All these pseudopotentials have to be Fourier transformed to obtain the coefficients $V_{\mathbf{K}-\mathbf{K}'}$, which are replaced in the OPW Schrödinger equation, which is in turn solved numerically.

5.4.1 Construction of pseudopotentials

Clearly, there is an enormous freedom in how pseudopotentials are constructed. Hoever, a sistematic, first-principles method to contruct pseudopotentials is highly desirable. Clearly, a requirements is that the pseudopotential should coincide with the actual potential outside the core region. But suppose tha the wave-function obtained with the pseudopotential differs from the actual one in the core region. That means that their respective charges will be distributed differently among core and valence regions, resulting in their norms being different. This charge difference is called *orthogonality hole*, and should be corrected for.

Different approaches have been used in the past construct pseudopotentials. This is a complicated problem and a whole topic to study separately.

See Thijssen's book for guidelines to build a self-consistent pseudo-potential.

5.4.2 Empirical pseudo-potentials

As we have seen beofre, we can write the pseudopotential as a Fourier series:

$$V(\mathbf{r}) = \sum_{\mathbf{K}} V(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{r}}; \;\; V_{\mathbf{K}} = \frac{1}{\sqrt{\Omega}} \int d^3 r V(\mathbf{r}) e^{-i\mathbf{K}\cdot\mathbf{r}} \tag{227}$$

In crystal structures that consist of more than one atom per unit cell, we need to introduce a *structure factor* $S_{\mathbf{K}}$, defined as

$$S_{\mathbf{K}} = \frac{1}{N} \sum_{i=1}^{N} e^{i\mathbf{K}\cdot\mathbf{r_i}}, \tag{228}$$

where the sum runs over all teh N atoms in the unit cell, at positions $\mathbf{r}_i$. The pseudopotential is teh expressed as a Fourier series, with the coefficients corrected by the structure factor as:

$$V_{\mathbf{K}} \rightarrow V_{\mathbf{K}} S_{\mathbf{K}}. \tag{229}$$

In crystals with a diamond structure there are two atoms at the positions $\mathbf{r}_1$ and $\mathbf{r}_2$ in the primitive unit cell. By taking the midpoint between the two atoms in the unit cell as origin, the positions of the atoms are given by $\mathbf{r}_1 = \frac{a_0}{8}(1,1,1) = \tau$ and $\mathbf{r}_2 = -\frac{a_0}{8}(1,1,1) = -\tau$. Thus, the structure factor is given by

$$S_{\mathbf{K}} = \frac{1}{2}\left(\exp(-i\mathbf{K}\cdot\tau) + \exp(i\mathbf{K}\cdot\tau)\right) = \cos(\mathbf{K}\cdot\tau) \tag{230}$$

In unstrained diamond structures the reciprocal lattice vectors in order of increasing magnitude are (in units of $\frac{2\pi}{a_0}$):

$$\begin{aligned}
\mathbf{K}_0 &= (0,0,0) && (231)\\
\mathbf{K}_3 &= (1,1,1),\ (\ \ 1,-1,1)\ ,\ldots\ ,(-1,-1,-1) && (232)\\
\mathbf{K}_4 &= (2,0,0),\ (-2,\ \ 0,0),\ \ldots\ ,(\ \ 0,\ \ 0,-2) && (233)\\
\mathbf{K}_8 &= (2,2,0),\ (\ \ 2,-2,0)\ ,\ldots\ ,(\ \ 0,-2,-2) && (234)\\
\mathbf{K}_{11} &= (3,1,1),\ (-3,\ \ 1,1)\ ,\ldots\ ,(-3,-1,-1) && (235)\\
& && (236)
\end{aligned}$$

Form factors with reciprocal lattice vectors larger than $K^2 > 11(\frac{2\pi}{a_0})^2$ are neglected, since typically $V_{\mathbf{K}}$ decreases as K^{-2} for large $\mathbf{K}$. Assuming that the atomic pseudopotentials are spherically symmetric $V(\mathbf{r}) = V(|\mathbf{r}|)$, the form factors only depend on the absolute value of the reciprocal lattice vector. The form factor belonging to $\mathbf{K}_0$ shifts the entire energy scale by a constant value, and can therefore be set to zero. The form factors belonging to the reciprocal lattice vectors $\mathbf{K}_3$ have an absolute value of $\sqrt{3}\cdot\frac{2\pi}{a_0}$ and are conventionally labeled V_3. Since the structure factor of the reciprocal lattice vectors $\mathbf{K}_4$ with magnitude $2\cdot\frac{2\pi}{a_0}$ vanishes,

$$\cos\left(\frac{2\pi}{a_0}\tau\cdot(\pm 2,0,0)\right) = \cos\left(\pm\frac{\pi}{2}\right) = 0\ , \tag{237}$$

the respective form factor V_4 does not enter the pseudopotential. Thus, only three pseudopotentials form factors V_3, V_8 and V_{11} are required to calculate the band structure.

Form Factor (Ry)	Si	Ge
V_3	-0.2241	-0.2768
V_8	0.0551	0.0582
V_{11}	0.0724	0.0152

In Table 5.4.2 the parameters employed in the empirical pseudopotential calculations are listed. They consist of three local form factors V_3, V_8, V_{11}.

5.5 The cellular (Wigner-Seitz) method

The TB model is too crude to be useful in calculations of actual bands, which are to be compared with experimental results. Now we shall consider some of the common methods employed in calculations of actual bands. The cellular method was the earliest method employed in band calculations by Wigner and Seitz. It was applied with success to the alkali metals, particularly to Na and K.

The method begins by observing that because of the Bloch relation, if we solve the Schrödinger equation in one unit cell, we know thie solution in the entire solid. However, we need to impose the boundary conditions that the function, and its derivative should vary continuously at the boundary between two neighboring cells.

In order to find the solution of the Schödinger equation, we assume that the electron, when in a particular cell, say A, is influenced by the potential of the ion in that cell only. The ions in other cells have a negligible effect on the electron in cell A because each of these cells is occupied, on the average, by another conduction electron which tends to screen the ion, thereby reducing its potential drastically. To ensure that the function ψ_k satisfies the Bloch form $\psi_k = e^{ikr} u_k$, it is necessary that u_k be periodic, i.e. u_k be the same on opposite faces of the cell.

The procedure is now clear in principle: We attempt to solve the Schrödinger equation in a single cell, using for $V(r)$ the potential of a free ion, which can be found from atomic physics. In Na, for instance, $V(r)$ is the potential of the ion core Na$^+$. It is still very difficult, however, to impose the requirements of periodicity on the function for the actual shape of the cell, and to overcome this difficulty Wigner and Seitz replaced the cell by a WS sphere of the same volume as the actual cell. The reason why this method is suitable for Na, is precisely because body-center cubic and face-centered cubic structures have a WS cells that are polyhedra that resemble spheres.

Using these simplifying assumptions concerning the potential and the periodic conditions, one then solves the Schrödinger equation numerically, since an analytical solution cannot usually be found.

Since the potential is spherically symmetric we write the wave function as

$$\psi_{lm}(\mathbf{r}) = Y_{lm}(\theta, \phi) R_l(r) \tag{238}$$

where Y_{lm} are spherical harmonics and the radial part satisfies the usual differential equation

$$R_l"(r) + \frac{2}{r}R_l'(r) + \frac{2m}{\hbar}\left(\epsilon - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)R(r) = 0 \tag{239}$$

Given the potential $V(r)$ and *any* value of ϵ there is a unique R_l that solves thsi equations and it is regular at the origin. These functions can be calculated numerically. Next, we write the wavefunction as:

$$\psi(\mathbf{r}, \epsilon) = \sum_{lm} A_{lm} Y_{lm}(\theta, \phi) R_l(r, \epsilon). \tag{240}$$

Now, we need to impose the following boundary conditions:

$$\begin{aligned} \psi(\mathbf{r}) &= e^{-i\mathbf{k}.\mathbf{R}}\psi(\mathbf{r}+\mathbf{R}), & (241) \\ \mathbf{n}\cdot\vec{\nabla}\psi(\mathbf{r}) &= -e^{-i\mathbf{k}.\mathbf{R}}\cdot\vec{\nabla}\psi(\mathbf{r}+\mathbf{R}). & (242) \end{aligned}$$

where both $\mathbf{r}$ and $\mathbf{R}$ are points on the surface of the cell, and $\mathbf{n}$ is the outward normal to the face of the WS cell. These boundary conditions introduces $\mathbf{k}$ into the equations and determine the discrete values of the energies for which these equations have a solution, *i.e* the energy bands $\epsilon = \epsilon(\mathbf{k})$.

Its is in the impositioon of these conditions that we make the major approximation. First, we take only as many terms in the expansion $\sum_{lm}$ as we are able to handle. Since there is only a finite number of coefficients in the expansions , we can only fit the boundary condition for a finite numbers of points on the cell. This leads to a set of k-dependent linear homogeneouos equations for the coefficients A_{lm}, that yield the wanted energies $\epsilon_n(\mathbf{k})$.

There are two ways to solve the k dependence:

- We fix $\mathbf{k}$ and we do a search to find the energies that correspond to zeroes in the determinant.

- We solve the differential equation for a given value of the energy ϵ and we look for the vector $\mathbf{k}$ at which the determinan vanishes. Provided that we have not chosen a value of ϵ in the middle of the gap, we can always find a solution.

5.5.1 Remarks about the cellular method

• Notice that the problem is equivalent to the atomic problem, except that the atomic boundary conditions (that the wave function vanishes at infinity) are replaced by the cellular boundary condition.

- It is questionable wether the potential representing an isolated atom is the best approximation for the periodic potential within the entire WS cell. In particular, this potential has discontinous derivatives when crossing to neighboring preimitive cells (the actual potential is quite flat and smooth in such regions).

5.6 The Muffin-tin potential

A potential that overcomes the objectionos with the cellular method is the Muffiin-tin potential, whcih is taken to represent an isolated ion within an spehere of radius r_0 around each lattice point, and taken to be constant elsewhere. The muffin-tin potential mitigates both problems, being flat in the intestitial region, and leading to matching conditions on a spherical, rather than a polyhedral surface.

Formally, the muffin-tin potential can be defined by:

$$U_{m-t}(\mathbf{r}) = \begin{cases} V(|\mathbf{r}-\mathbf{R}|) & \text{when } |\mathbf{r}-\mathbf{R}| < r_0 \\ \text{constant} & \text{when } |\mathbf{r}-\mathbf{R}| \geq r_0 \end{cases} \tag{243}$$

where r_0 is less than half the distance between neighboring sites.

5.7 The Augmented plane-wave method (APW)

The APW method was developed by Slater in 1937. Since the effective crystal potential was found to be constant in most of the open spaces between the cores, the APW method begins by assuming such a muffin-tin potential. The potential is that of a free ion at the core, and is strictly constant outside the core. The wave function for the wave vector $\mathbf{k}$ is now taken to be

$$\psi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{k}\cdot\mathbf{r}} & \text{when } |\mathbf{r}-\mathbf{R}| \geq_0 \\ \text{atomic function} & \text{when } |\mathbf{r}-\mathbf{R}| < r_0 \end{cases} \tag{244}$$

where r_0 is the core radius. Outside the core the function is a plane wave because the potential is constant there. Inside the core the function is atom-like, and is found by solving the appropriate free-atom Schrödinger equation. Also, the atomic function is chosen such that it joins continuously to the plane wave at the surface of the sphere forming the core; this is the boundary condition here.

Notice that there is no constraint relating $\mathbf{k}$ and ϵ for a plane-wave, since we have $\epsilon = \hbar^2 k^2/2m$. It is the boundary conditions that determine the value of $\mathbf{k}$ for a given ϵ.

5.7.1 Matching the boundary conditions

We have defined our APW as:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{k}\cdot\mathbf{r}} & \text{when } |\mathbf{r}-\mathbf{R}| \geq r_0 \\ \sum_{lm} A_{lm} Y_{lm}(\theta,\phi) R_l(r,\epsilon). & \text{when } |\mathbf{r}-\mathbf{R}| < r_0 \end{cases} \tag{245}$$

If an eigenfunction would be discontinuous, its kinetic energy would not be well-defined. Such a situation can therefore never happen, and we have to require that the plane wave outside the sphere matches the function inside the sphere over the complete surface of the sphere (in value, not in slope). That seems a weird thing to do: a plane wave is oscillating and has a unique direction built in, how can it match another function based on spherical harmonics over the entire surface of a sphere? To see how this is possible, we expand the plane wave in spherical harmonics:

$$\exp\left(i\mathbf{k}\cdot\mathbf{r}\right) = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} i^l\, j_l(kr) Y^*_{lm}(\theta_{\mathbf{k}},\phi_{\mathbf{k}}) Y_{lm}(\theta,\phi) \tag{246}$$

where θ,ϕ,r correspond to the polar representation of $\mathbf{r}$ and $\theta_{\mathbf{k}}$,$\phi_{\mathbf{k}}$,k to $\mathbf{k}$. To keep the problem tractable, we cut all the expansions in lm to a finite value of l. $j_l(r)$ is the Bessel function of order l. Requiring this at the sphere boundary means that all the coefficients of Y_{lm} have to be equal for both parts of the function at the boundary. Thsi conditiono fixes the A_{lm} and we obtain:

$$\psi^{APW}_{\mathbf{k}}(\mathbf{r}) = 4\pi \sum_{lm} i^l \left[\frac{j_l(kr_0)}{R_l(r_0)}\right] R_l(r) Y^*_{lm}(\theta_{\mathbf{k}},\phi_{\mathbf{k}}) Y_{lm}(\theta,\phi) \tag{247}$$

for the function inside the sphere.

The APW function is no a solution to the Scrödinger equation, but they are appropriate for expanding the actual wave function. The APW method tries to approximate the correct solution to the crystal by a superposition of APW's, all with the same energy. For any reciprocal lattice vector $\mathbf{K}$, the APW satisfies the Bloch condition with wave vector $\mathbf{k}$, but for the entire wavefunctioon to be of the Bloch form we need the expansion of $\psi_{\mathbf{k}}(\mathbf{r})$

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{K}} c_{\mathbf{K}} \psi^{APW}_{\mathbf{k}+\mathbf{K},\epsilon(\mathbf{k})}(\mathbf{r}) \tag{248}$$

where the sum is over all the reciprocal lattice vectors.

The hope is that we swill need only a small number of APW's to approximate the full Schrödinger euqation in the interstitial region and at the boundary. In practice, as many as a several hundreeds can be used. By the time we do this, the energy does not change much, as more APW's are added, and we achieve convergence.

All the APW have to be evaluated at the same energy. The coefficients are given, again, by solving the generalized eigenvalue equation

$$Hc = ESc \tag{249}$$

where the elements of H and S have very complicated expressions.

The most remarkable aspect of this equation is, that even though is looks like an ordinary eigenvalue problem, the marix elements depend on energy! To solve the problem it is convenient to work a fixed energy, and look for the k's at which the following secular expresion is satisfied:

$$(H - ES)c = 0 \tag{250}$$

Another possibility, is to fix the momentum $\mathbf{k}$, and define a fine energy mesh, and look for the zeros of the determinant $|H - ES|$.

5.7.2 Matrix elements

$$(H-ES)_{ij} = \langle \mathbf{k}+\mathbf{K}_i | H - ES | \mathbf{k}+\mathbf{K}_j \rangle = -EA_{ij} + B_{ij} + \sum_{l=0}^{l_{max}} C_{ijl} \frac{R_l'(r_0)}{R_l(r_0)}. \tag{251}$$

$$\begin{aligned} A_{ij} &= \frac{-4\pi r_0^2}{\Omega} \frac{j_1(|\mathbf{K}_i - \mathbf{K}_j| r_0)}{|\mathbf{K}_i - \mathbf{K}_j|} + \delta_{ij} && (252) \\ B_{ij} &= \frac{\hbar^2}{2m} A_{ij} (\mathbf{q}_i \cdot \mathbf{q}_j) && (253) \\ C_{ijl} &= (2l+1) \frac{2\pi r_0^2}{\Omega} P_l \left(\frac{\mathbf{q}_i \cdot \mathbf{q}_j}{k_i k_j} \right) j_l(q_i r_0) j_l(q_j r_0) && (254) \end{aligned}$$

where Ω is the volume of the unit cell, and P_l is the Legendre polynomial, and $\mathbf{q}_i = \mathbf{K}_i + \mathbf{k}$.

5.7.3 Some remarks about the APW method

- Note that the wavefunction in general will have discontinous derivatives on the boundary between the interstitial and atomic regions.
- In the APW method the augmenting function R_l corresponds to the exact muffin-tin potential eigenstate of eigenenergy . Because of this energy dependence of the function R_l the eigenvalue problem will be non-linear in energy and has to be solved iteratively. This is, however, computationally very costly. On the other hand, any eigenstate of a different eigenenergy will be poorly described without adapting . To overcome this problem linearized versions of the APW method have been developed, where the energy is set to a fixed value and the basis functions are modified to gain extra flexibility to cover a larger energy region around their linearization energy. These methods are the linearized APW method (LAPW) and the APW+ local orbitals (APW+lo).

5.8 The LAPW method

The traditional way of linearizing the APW method is the LAPW method, which was developed in the beginning of the 1970s. In this approach the basis functions are expanded in the same way as in Eq. (245) in the interstitial, but inside the muffin- tin the basis functions do not only depend on $R_l(r, \epsilon)$, but also on its derivative $\dot{R}_l(r, \epsilon) \equiv \partial R_l / \partial \epsilon$.

The idea is that the radial wavefunction can be approximated well around an energy of interest by a linearization of the form:

$$R(r, \epsilon) = R(r, \epsilon_p) + (\epsilon - \epsilon_p)\dot{R}(r, \epsilon_p), \tag{255}$$

where ϵ_p is some reference energy, or pivot energy.

The LAPW wavefunction then reads

$$\psi_{\mathbf{k}}(\mathbf{r}) = \begin{cases} e^{i\mathbf{k}\cdot\mathbf{r}} & \text{when } |\mathbf{r}-\mathbf{R}| \geq r_0 \\ \sum_{lm} \left[A_{lm} R_l(r, \epsilon_p) + B_{lm} \dot{R}(r, \epsilon_p)\right] Y_{lm}(\theta, \phi) & \text{when } |\mathbf{r}-\mathbf{R}| < r_0 \end{cases} \tag{256}$$

The remarkable aspect of this expression is that the wavefunction no longer depends on the energy. The price we pay is in the accuracy of the wavefunction inside the MT sphere.

We end up with a generalized eigenvalue problem with energy-independent overlap and Hamiltonian matrices. these matrices are reliables within some range around the pivot energy.

5.9 Adding electron-electron interactions

The exchange correlations and Hartree potenatials are density-dependent and add a self-consistency ingredient to the soup. Now, the Hamiltonian becomes a Kohn-Sham Hamiltonian. After diagonalizing teh Hamiltonian, we obtain teh Fourier compotents of the wave-functions. Then, we can calculate the density in real-space and reciprocal space.

The exchange-correlation potentials is given as the derivative of the energy with respect to the density n. It must be calculated in real space, and then Fourier transformed to that it can be added to the Hamiltonian in momentum representation.

The Hartree potential

$$V_H(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' \tag{257}$$

can be Fourier transformed to give

$$V_H(\mathbf{K} - \mathbf{K}') = \frac{4\pi}{|\mathbf{K} - \mathbf{K}'|^2} n(\mathbf{K} - \mathbf{K}'). \tag{258}$$

6 Random sequences

Imagine a bingo draw, where numbered balls are picked randomly. If you want to reproduce this process with a computer, you will find that it is not as easy as you might think. Computing is completely deterministic by nature, and reproducing or simulating naturally random processes is a particularly delicate matter.

The problem is how to use a computer to generate random numbers. In fact, this is impossible! We can program a computer to generate a sequence of numbers, following certain law. Although the output values of this sequence might look random (according to some rules that we will discuss in this section), the existence of a deterministic law behind them is telling us that precisely, these are not random numbers at all!

We define a sequence of numbers $\{r_1, r_2, ...r_n\}$ as "random" if there are no correlations among the numbers in the sequence. A random sequence can have a distribution, *i. e.* the probability of a number to appear in the sequence would correspond to some distribution. If the distribution is uniform, all numbers are equally probable to appear. Mathematically, the likehood of a number to occur is described by a distribution function $P(r)$. This means that the probability of finding r_i in the interval $[r, r+dr]$ is given by $P(r)dr$. The usual random number generators provided by compilers or libraries generate a uniform distribution between 0 and 1, that means $P(r) = 1$. Ideally this numbers have equal probability, and it is independent of the previous one.

The computer, the sequences are "pseudo-random" because knowing a number r_m and the preceeding r_i, we can predict the next one r_{m+1}. This is evident in the correlations. Some sophisticated psudo-random number generators do a good job hiding this fact from our eyes, although if you look hard enough, you will eventually figure it out.

6.1 Pseudo-random number generators

In this section we will simply review some possible alternatives for pseudo-random number generators. These go from the simplest "congruential" or "power residue" algorithm to more sophisticated ones that can be found in the literature. We will limit ourselves to understand this simple example. We want to generate a sequence $\{r_i\}$ over an interval $[0, M-1]$. You multiply the previous random number r_i by a constant a, add on another constant c, take the modulus by M, and then keep just the fractional part, the reminder, as the next rendom number r_{i+1}:

$$r_{i+1} = (ar_i + c)\mathrm{modM} = \mathrm{remainder}\left(\frac{\mathrm{ar_i + c}}{\mathrm{M}}\right).$$

The value r_1 has to be supplied by the user, and it is called the "seed" of the sequence. The sequence will be uniquely pre-determined by the seed.

As an example, let us pick $c = 1$,$a = 4$,$M = 9$ and $r_1 = 3$. We obtain the sequence:

$$\begin{aligned} r_1 &= 3, && (259) \\ r_2 &= (4 \times 3 + 1)\mathrm{mod}9 = 4, && (260) \\ r_3 &= (4 \times 4 + 1)\mathrm{mod}9 = 8, && (261) \\ r_4 &= (4 \times 8 + 1)\mathrm{mod}9 = 6, && (262) \\ , 7, 2, 0, 1, 5, 3, ... & && (263) \end{aligned}$$

We get a sequence of length $M = 9$ after which the entire sequence repeats. This means that the "period" of the sequence is $M - 1$. If we want the numbers in the range $[0, 1]$ we would divide these values by M. This algorithm is extremely simple and portable, and it's particularly suitable for simple applications. As we have seen, the longer the M, the longer the "period" of the sequence. Using large integer raises the problem of protability. Most processors use 32-bit representation for integers (some 64). This limits the largest possible integer that can be used. However, there are ways to work around this issue.

The C++ Standard Library provides a psuedo-random number generator. It provides a function to initialize the seed of the sequence:

srand(size_t seed); and the actual call to retrieve a new random number rand();

The generator provides a sequence between 0 and RAND_MAX, which is a large integer that deppends on the implementation. A common way to generate independent sequences is to use the internal clock of the computer to generate a relatively random seed.

For more on random number generators read Knuth, Numerical Recipes.

6.2 Testing for randomness and uniformity

Since the random numbers are generated according to a deterministic rule, the numbers in the sequence must be correlated in a certain way. This can affect a simulation that assumes random events.Therefore it is wise to test a generator before you use it.

6.2.1 Moments

The $k-th$ moment of a distribution is defined as:

$$\langle x^k \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i^k. \tag{264}$$

If the numbers are distributed with a uniform probability distribution $P(x)$, then (264) must correspond to the moment of P:

$$\int_0^1 x^k P(x) dx \sim \frac{1}{k+1}.$$

If this holds for your generator, then you know that the distribution is uniform. If the deviation from this varies as $1/\sqrt{N}$, then you also know that the distribution is random.

6.2.2 Autocorrelation

Another simple test determines the near-neighbor correlation in your random sequence by taking the sume of products at a "distance" m:

$$C(m) = \langle x_i x_{i+m} \rangle = \frac{1}{N} \sum_{i=1}^{N} x_i x_{i+m}. \tag{265}$$

If your random numbers are distributed with a joint probability distribution $P(x_i, x_{i+m})$ and are independent and uniform, then (265) must compare to the integral:

$$\int_0^1 dx \int_0^1 dy P(x,y) xy.$$

6.2.3 Visual test

If you plot the points (r_{2i}, r_{2i+1}) and you notice some sort of regularity, the sequence is not random. If the points are random, they should uniformly fill a square with no discernible pattern.

6.2.4 Statistical errors

If you run a simulation using a pesudo-random generator, you may expect your measurements (of some quantity, and observable for instance) to be distributed according to some statistics. If your results do not satisfy these statistics, then you should pick another generator. If you know a good random-number generator (you usually try to avoid this kind because they are time-consumming), it is a good idea to compare your results for a short run, to see is they agree or not.

6.3 Non-uniform random distributions

In th eprevious section we learned how to generate random deviates with a uniform probability distribution in an interval $[a, b]$. This distributioon is normalized, so that

$$\int_a^b P(x)dx = 1.$$

Hence, $P(x) = 1/(b - a)$.

Now, suppose that we generate a sequence $\{x_i\}$ and we take some function of it to generate $\{y(x_i)\} = \{y_i\}$. This new sequence is going to be distributed according to some probaility density $P(y)$, such that

$$P(y)dy = P(x)dx$$

or

$$P(y) = P(x)\frac{dx}{dy}.$$

If we want to generate a desired normalized distribution $P(y)$, we need to solve the differential equation:

$$\frac{dy}{dy} = P(y).$$

But the solution of this is

$$x = \int_0^y P(y')dy' = F(y).$$

Therefore,

$$y(x) = F^{-1}(x), \tag{266}$$

where F^{-1} is the inverse of F.

6.3.1 Exponential distribution

As an example, let us take $y(x) = -\ln(x)$ with $P(x)$ representing a uniform distribution in the interval $[0,1]$. Then

$$P(y) = \frac{dx}{dy} = e^{-y},$$

which is distributed exponentially. This distribution occurs frequantly in real problems such as the readioactive decay of nuclei. You can also see that the quantity y/λ has the distribution $\lambda e^{-\lambda y}$.

6.4 von Neumann rejection

A simple and ingenious method for generating random points with a probability distribution $P(x)$ was deduced by von Neumann. Draw a plot with you probability distribution, and on the same graph, plot another curve $f(x)$ which has finite area and lies everywhere above your original distribution. We will call $f(x)$ the "comparison function". Generate random pairs (x_i, y_i) with uniform distribution inside $f(x)$. Whenever the point lies inside the area of the original probability, we accept it, otherwise, we reject it. All the accepted points will be uniformly distributed within the original area, and therefore will have the desired distribution. The fraction of points accepted/rejected will deppend on the ratio between the two areas. The closer the comparison function $f(x)$ resembles $P(x)$, the more points will be accepted. Ideally, for $P(x) = f(x)$, all the points will be accepted, and none rejected. However, in practice, this is not always possible, but we can try to pick $f(x)$ such that we minimize the fraction of rejected points.

It only remains how to pick a number with probability $f(x)$. For this purpose, we utilize the method shown in the previous section, using a function whose indefinite intergral is know analitically, and is also analitically invertible. We then pick a random number x and retrieve the corresponding $y(x)$ according to (266). Then, we generate a second random number and we use the rejection criterion.

An equivalent procedure consists of picking the second number between 0 and 1 and accept or reject according to wether is it respectively less than or greater than the ratio $P(x)/f(x)$

6.5 Random walk methods: the Metropolis algorithm

Suppose that we want to generate random variables according to an arbitrary probability density $P(x)$. The Metropolis algorithm produces a "random walk" of points $\{x_i\}$ whose asymptotic probability approaches $P(x)$ after a large number of steps. The random walk is defined by a "transition probability" $w(x_i \to x_j)$ for one value x_i to another x_j in order that the distribution of points x_0, x_1, x_2, ... converges to $P(x)$. In can be shown that it is sufficient (but not necessary) to satisfy the "detailed balance" condition

$$p(x_i)w(x_i \to x_j) = p(x_j)w(x_j \to x_i). \tag{267}$$

This relation dos not specify $w(x_i \to x_j$ uniquely. A simple choice is

$$w(x_i \to x_j) = \min\left[1, \frac{P(x_j)}{P(x_i)}\right]. \tag{268}$$

This choice can be described by the following steps. Suppose that the "random walker" is a position x_n. To generate x_{n+1} we

1. choose a trial position $x_t = x_n + \delta_n$, where the δ_n is a random number in the interval $[-\delta, \delta]$.
2. Calculate $w = P(x_t)/P(x_n)$.
3. If $w \geq 1$ we accept the change and let $x_{n+1} = x_t$.
4. If $w \leq 1$, generate a random number r.
5. If $r \leq w$, accept the change and let $x_{n+1} = x_t$.
6. If the trial change is not accepted, the let $x_{n+1} = x_n$.

It is necessary to sample a number of points of the random walk before the asymptotic probability $P(x)$ is attained. How do we choose the "step size" δ? If δ is too large, only a small fraction of changes will be accepted and the sampling will be inefficient. If δ is too small, a large number will be accepted, but it would take too long to sample $P(x)$ over the whole interval of interest. Ideally, we want at least 1/3-1/2 of the trial steps to be accepted. We also want to choose x_0 such that the distribution $\{x_i\}$ converges to $P(x)$ as quickly as possible. An obvious choice is to begin the random walk at the point where $P(x)$ is maximum.

6.5.1 Exercise 9.1: The Gaussian distribution

1. Use the Metropolis algorithm to generate a Gaussian distribution $P(x) = A \exp\left(-x^2/2\sigma^2\right)$. Is the numerical value of the normalization constant A relevant? Determine the qualitative dependence of the acceptance ratio and the equilibrium time on the maximum step size δ. One possible criterion for equilibrium is that $\langle x^2 \rangle \approx \sigma^2$. For $\sigma = 1$, what is a reasonable choice of δ? (choose $x_0 = 0$.)

2. Plot the asymptotic probability distribution generated by the Metropolis algorithm.

7 Monte Carlo integration

Imagine that we want to measure the area of a pond with arbitrary shape. Suppose that this pond is in the middle of a field with known area A. If we throw N stones randomly, such that they land within the boundaries of the field, and we count the number of stones that fall in the pond N_{in}, the area of the pond will be approximately proportional to the fraction of stones that make a splash, multiplied by A:

$$A_pond = \frac{N_{in}}{N} A.$$

This simple procedure is an example of the "Monte Carlo" method.

7.1 Simple Monte Carlo integration

More generaly, imagine a rectangle of height H in the integration interval $[a, b]$, such that the function $f(x)$ is within its boundaries. Compute n pairs of random numbers (x_i, y_i) such that they are uniformly distributed inside this rectangle. The fraction of points that fall within the area contained below $f(x)$, *i. e.*, that satisfy $y_i \leq f(x_i)$ is an estimate of the ratio o fthe integral of $f(x)$ and the area of the rectangle. Hence, the estimate of the integral will be given by:

$$\int_a^b f(x)dx \simeq I(N) = \frac{N_{in}}{N} H(b-a). \tag{269}$$

Another Monte Carlo procedure is based on the definition:

$$\langle g \rangle = \frac{1}{(b-a)} \int_a^b f(x)dx. \tag{270}$$

In order to determine this average, we sample the value of $f(x)$:

$$\langle f \rangle \simeq \frac{1}{N} \sum_{i=1}^{N} f(x_i),$$

where the N values x_i are distributed unformly in the interval $[a, b]$. The integral will be given by

$$I(N) = (b-a)\langle f \rangle.$$

7.2 Monte Carlo error analysis

The Monte Carlo method clearly yields approximate results. The accuracy deppends on the number of values N that we use for the average. A possible measure of the error is the "variance" σ^2 defined by:

$$\sigma^2 = \langle f^2 \rangle - \langle f \rangle^2, \tag{271}$$

where

$$\langle f \rangle = \frac{1}{N} \sum_{i=1}^{N} f(x_i)$$

and

$$\langle f^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} f(x_i)^2.$$

The "standard deviation" is σ. However, we should expect that the error decreases with the number of points N, and the quantity σ defines by (271) does not. Hence, this cannot be a good measure of the error.

Imagine that we perform several measurements of the integral, each of them yielding a result I_n. Thes values have been obtained with different sequences of N random numbers. According to the central limit theorem, these values whould be normally dstributed around a mean $\langle I \rangle$. Suppouse that we have a set of M of such measurements I_n. A convenient measure of the differences of these measurements is the "standard deviation of the means" σ_M:

$$\sigma_M^2 = \langle I^2 \rangle - \langle I \rangle^2, \tag{272}$$

where

$$\langle I \rangle = \frac{1}{M} \sum_{n=1}^{M} I_n$$

and

$$\langle I^2 \rangle = \frac{1}{M} \sum_{n=1}^{M} I_n^2.$$

Although σ_M gives us an estimate of the actual error, making additional meaurements is not practical. instead, it can be proven that

$$\sigma_M \approx \sigma/\sqrt{N}. \tag{273}$$

This relation becomes exact in the limit of a very large number of measurements. Note that this expression implies that the error decreases withthe squere root of the number of trials, meaning that if we want to reduce the error by a factor 10, we need 100 times more points for the average.

Exercise 10.1: One dimensional integration

1. Write a program that implements the "hit and miss" Monte Carlo integration algorithm. Find the estimate $I(N)$ for the integral of

   $$f(x) = 4\sqrt{1-x^2}$$

   as a function of N, in the interval $(0,1)$. Choose $H = 1$, and sample only the x-dependent part $\sqrt{1-x^2}$, and multiply the result by 4. Calculate the difference between $I(N)$ and the exact result π. This difference is a measure of the error associated with the Monte Carlo estimate. Make a log-log plot of the error as a function of N. What is the approximate functional deppendece of the error on N for large N?

2. Estimate the integral of $f(x)$ using the simple Monte Carlo integration by averaging over N points, using (270), and compute the error as a function of N, for N upt to 10,000. Determine the approximate functional deppendence of the error on N for large N. How many trials are necessary to determine I_N to two decimal places?

3. Perform 10 measurements $I_n(N)$, with $N = 10,000$ using different random sequences. Show in a table the values of I_n and σ according to (270) and (271). Use (272) to estimate the standard deviation of the means, and compare to the values obtained from (273) using the 100,000 values.

4. To verify that your result for the error is independent of the number of sets you used to divide your data, repeat the previous item grouping your results in 20 groups of 5,000 points each.

Exercise 10.2: Importance of randomness

To examine the effects of a poor random number generator, modify your program to use the linear congruential random number generator using the perameters $a = 5$, $c = 0$ and the seed $x_1 = 1$. Repeat the integral of the previous exercise and compare your results.

7.3 Variance reduction

If the function being integrated does not fluctuate too much in the interval of integration, and does not differ much from the average value, then the standard Monte Carlo mean-value method should work well with a reasonable number of points. Otherwise, we will find that the variance is very large, meaning that some points will make small contributions, while others will make large contributions to the integral. If this is the case, the algorithm will be very inefficient. The method can be improves by splitting the function $f(x)$ in two $f(x) = f_1(x) + f_2(x)$, such that the integral of $f_1(x)$ is known, and $f_2(x)$ as a small variance. The "variance reduction" technique, consists then in evaluating the integral of $f_2(x)$ to obtain:

$$\int_a^b f(x)dx = \int_a^b f_1(x)dx + \int_a^b f_2(x)dx = \int_a^b f_1(x)dx + J.$$

7.4 Importance Sampling

Imagine that we want to sample the function $f(x) = e^{-x^2}$ in the interval $[0, 1]$. It is evident that most of our points will fall in the region where the value of $f(x)$ is very small, and therefore we will need a large number of values to achieve a decent accuracy. A way to improve the measurement by reducing the variance is obtained by "importance sampling". As the name says, the idea is to sample the regions with larger contributions to the integral. For this goal, we introduce a probability distribution $P(x)$ normalized in the interval of integration

$$\int_a^b P(x)dx = 1.$$

Then, we can rewrite the integral of $f(x)$ as

$$I = \int_a^b \frac{f(x)}{P(x)} P(x)dx \tag{274}$$

We can evaluate this integral, by sampling according to the probability distribution $P(x)$ and evaluating the sum

$$I(N) = \frac{1}{N} \sum_{i=1}^{N} \frac{f(x_i)}{P(x_i)}. \tag{275}$$

Note that for the uniform case $P(x) = 1/(b-a)$, the expression reduces to (270).

We are free to choose $P(x)$ now. We wish to do it in a way to reduce and minimize the variance of the integrand $f(x)/P(x)$. The way to to this is picking a $P(x)$ that mimics $f(x)$ where $f(x)$ is large. if we are able to determine an apropiate $p(x)$, the integrand will be slowly varying, and hence the variance will be reduced. Another consideration is that the generation of points according to the distribution $P(x)$ should be a simple task. As an example, let us consider again the integral

$$I = \int_0^1 e^{-x^2} dx.$$

A reasonable choice for a weigh function is $P(x) = Ae^{-x}$, where A is a normalization constant.

Notice that for $P(x) = f(x)$ the variance is zero! This is known as the zero variance property.

Exercise 10.3: Importance sampling

1. Choose the weight function $P(x) = e{-}x$ and evaluate the integral:

$$\int_0^\infty x^{3/2} e^{-x} dx.$$

2. Choose $P(x) = e^{-ax}$ and estimate the integral

$$\int_0^\pi \frac{dx}{x^2 + \cos^2 x}.$$

   Determine the value of a that minimizes the variance of the integral.

Exercise 10.4: The Metropolis algorithm

Use the Metropolis algorithm to sample points according to a ditribution and estimate the integral

$$\int_0^4 x^2 e^{-x} dx,$$

with $P(x) = x^2 e^{-x}$ for $0 \leq x \leq 4$. Plot the number of times the walker is at points x_0, x_1, x_2, ... Is the integrand sampled uniformly? If not, what is the approximate region of x where the integrand is sampled more often?

8 Monte Carlo Simulation

8.1 The Canonical Ensemble

Most physical systems are not isolated, bu exchange energy with the environment. Since the system is very small compared to the environment, we consider that the environment acts effectively as a heat reservoir or heat bath at a fixed temperature T. If a small system is put in thermal contact with the heat bath, it will reach thermal equilibrium exchanging energy until the system attains the temperature of the bath.

Imagine an infinitely large number of mental copies of the system and the heat bath. The probability P_s that the system is found in a microstate s with energy s is given by:

$$P_s = \frac{1}{Z} e^{-E_s/k_B T}, \tag{276}$$

where Z is the normalization constant. This corresponds to the canonical ensemble. Since $\sum P_s = 1$, we have

$$Z = \sum_s e^{-E_s/k_B T}, \tag{277}$$

where the sum is over all the possible microstates of the system. This equation defines the "partition function" of the system.

We can use (276) to obtain the ensemble average of physical quantities of interest. For instance, the mean energy is given by:

$$\langle E \rangle = \sum_s E_s \, P_s = \frac{1}{Z} \sum_s E_s \, e^{-\beta E_s},$$

with $\beta = 1/k_B T$.

8.2 The Metropolis algorithm

we wan to obtain an estimate for the mean value of an observable A:

$$\langle A \rangle = \sum_s A_s e^{-\beta E_s} / \sum_s e^{-\beta E_s},$$

where E_s and A_s are the values of the energy and the quantity A in the configuration s. The idea of using Monte Carlo consists in sampling a subset of configuration and approximating the average by the mean over the sample:

$$\langle A \rangle \simeq \sum_s^m A_s e^{-\beta E_s} / \sum_s^m e^{-\beta E_s},$$

where the sampling is over m configurations.

A crude Monte Carlo procedure is to generate a configuration at random, calculate E_s and A_s, and the contributions of this configuration to the sums. This is equivalent to the "hit and miss" Monte Carlo method for evaluating integrals. We have seen that this approach is very inefficient, because the configurations generated would likely be very improbable and contribute very little to the sum. Instead, we want to generate a sample of configurations that are *important*, *i. e.* have large contributions to the sums. This is precisely the equivalent to "importance sampling". Hence, we need to generate the configurations according to a probability distribution. In this case, the most convenient one is not other than the Boltzmann probability itself P_s (276). Since we will average over the m configurations generated with this probability, we must use the expression:

$$\langle A \rangle \simeq \sum_s^m \frac{A_s}{P_s} e^{-\beta E_s} / \sum_s^m \frac{1}{P_s} e^{-\beta E_s} = \frac{1}{m} \sum_s^m A_s$$

The idea of the Monte Carlo algorithm consists in performing a random walk over the space of configurations. The walker "hops" from a configuration i to another j using the "transition probability"

$$W = \min \left(1, \frac{P_j}{P_j} \right).$$

Replacing by the corresponding expression, we obtain:

$$W = \min \left(1, e^{-\beta(E_j - E_i)} \right).$$

Since we are only interested in the ratio P_j/P_j, it is not necessary to know the normalization constant Z. Although we have picked this expression for the transition probability W, is not the only choice. It can be shown that the only requirement is that W satisfies the "detailed balance" condition:

$$W(i \rightarrow j) e^{-\beta E_i} = W(2 \rightarrow j) e^{-\beta E_j}.$$

Another comon choice in the literature is given by:

$$W(i \to j) = \frac{1}{e^{-\beta(E_j - E_i)} + 1}.$$

Note that if $\Delta E = 0$, then $W = 1/2$ and the trial configuration has an equal probability of being accepted.

The pseudocode for a Monte Carlo simulation can be outlined as follows:

1. Establish an initial configuration.
2. Make a random trial change in the configuration. For example, choose a spin at random and try to flip it. Or choose a particle at random and attempt to displace it a random distance.
3. Compute the change in the energy of the system ΔE due to the trial change.
4. If $\Delta e \leq 0$, accept the new configuration and go to step 8.
5. If ΔE is positive, compute the "transition probability" $W = e^{-\beta \Delta E}$.
6. Generate a random number r in the interval $[0, 1]$.
7. If $r \leq W$, accept the new configuration; otherwise retain the previous configuration.
8. Repeat steps (2) to (8) to obtain a sufficient number of configurations or "trials".
9. Compute averages over configurations which are statistically independent of each other.

Exercise 13.1: Classical gas in 1D

1. simulate an ideal gas of N particles in 1D. Choose $N = 20$, $T = 100$ and 200 MC steps. Give all the particles the same initial velocity $v_0 = 10$. Determine the value of the maximum velocity change Δv so that the acceptance ratio is approximately 50%. What is the mean kinetic energy and mean velocity of the particles?

2. We might expect that the total energy of an ideal gas to remain constant since the particles do not interact with each other and hence they cannot exchange energy directly. What is the initial value of the energy of the system? Does it remain constant? If it does not, explain how the energy changes. Explain why the measured mean particle velocity is zero even though the initial particle velocities are not zero.

3. What is a simple criterion for "thermal equilibrium"? Estimate the number of Monte Carlo steps per particle necessary for the system to reach thermal equilibrium. What choice of the initial velocities allows the system to reach thermal equilibrium at temperature T as quickly as possible?

4. Compute the mean energy per particle for $T = 10$, 100 and 400. In order to compute the averages after the system has reached thermal equilibrium, start measuring only after equilibrium has been achieved. Increase the number of Monte Carlo steps until the desired averages do not change appreciably. What is the approximate number of warmup steps for $N = 10$ and $T = 100$, and for $N = 40$ and $T = 100$? If the number of warmup steps is different in the two cases, explain the reason for this difference.

5. Compute the probability $P(E)dE$ for the system of N particles to have a total energy between E and $E + dE$. Do you expect $P(E)$ to be proportional to $e^{-\beta E}$? Plot $P(E)$ as a function of E and describe the qualitative behavior of $P(E)$. Doe s the plot of $\ln(P(E))$ yield a straight line?

6. Compute the mean energy for $T = 10$, 20, 30, 90, 100 and 110 and estimate the heat capacity.

7. Compute the mean square energy fluctuations $\langle \Delta E^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$ for $T = 10$ and $T = 40$. Compare the magnitude of the ratio $\langle \Delta E^2 \rangle / T^2$ with the heat capacity determined in the previous item.

8.3 The Ising model

Consider a lattice with N sites, where each site i can assume two possible states $s_i = +1, -1$, or spin "up" and spin "down". A particular configuration or microstate of the lattice is specified by the set of variables $\{s_1, s_2, ...s_N\}$ for all lattice sites.

Now we need to know the dependence of the energy E of a given microstate, according to the configuration of spins. The total energy in the presence of a uniform magnetic field is given by the "Ising model":

$$E = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_{i=1}^{N} s_i, \tag{278}$$

where the first summation is over all nearest neighbor pairs and the second summation is over all the spins of the lattice. The "exchange constant" J is a measure of the strength of the interaction between nearest neighbor spins. If $J > 0$, the states with the spins aligned $\uparrow\uparrow$ and $\downarrow\downarrow$ are energetically favored, while for $J < 0$ the configurations with the spins antiparallel $\uparrow\downarrow$ and $\downarrow\uparrow$ are the ones that are preferred. In the first case, we expect that the state with lower energy is "ferromagnetic", while in the second case, we expect it to be "antiferromagnetic". If we subject the system to a uniform magnetic field h directed upward, the spins $\uparrow$ and $\downarrow$ possess and additional energy $-h$ and $+h$ respectively. Note that we chose the units of h such that the magnetic moment per spin is unity.

Instead of obeying Newton's laws, the dynamics of the Ising model corresponds to "spin flip" processes: a spin is chosen randomly, and the trial change corresponds to a flip of the spin $\uparrow\rightarrow\downarrow$ or $\downarrow\rightarrow\uparrow$.

8.3.1 Boundary conditions

Since we are interested in the properties of an infinite system, we have to consider the boundary conditions. The simplest case corresponds to "free boundary condition", where the spins at sites 1 and N are open ends and have one interaction each. In general a better choice is periodic boundary conditions, where sites 1 and N interact with each other closing a loop. In this situation, the chain has the topology of a ring, and all the spins have the same number of interactions. We also say that there is translational invariance, since the origin can be picked arbitrarily.

8.3.2 Physical quantities

The net magnetic moment or "magnetization' M is given by

$$M = \sum_{i=1}^{N} s_i. \tag{279}$$

Usually we are interested in the average $\langle M \rangle$ and the fluctuations $\langle M^2 \rangle - \langle M \rangle^2$ as a function of the temperature of the system and the applied magnetic field.

Exercise: One-dimensional Ising model

1. Choose $N = 20$, $T = 1.0$, and all the spins initially pointing "up" as the initial state. Calculate the energy after each step, and estimate the number of steps for the system to reach equilibrium.

2. Pick all the spins initially poiting randomly. Estimate the time that takes for the system to reach equilibrium.

3. Choose $N = 20$ and equilibrate the system for 100 MC steps. Use at least 200 MC steps to determine the mean energy $\langle E \rangle$ and magnetization $\langle M \rangle$ as a function of T in the range $T = 0.5$ to 5.0. Plot $\langle E \rangle$ as a function of T ans discuss its qualitative features. Compare your computed results for the mean energy to the exact values:

   $$\langle E \rangle = -N \tanh \left(\frac{J}{k_B T} \right).$$

   What are yout results for $\langle M \rangle$? Do they depend on the initial configuration?

4. Is the acceptance ratio and increasing or decreasing function of T? Does the Metropolis algorithm become more or less efficient at low temperatures?

8.4 Simulation of the 2D Ising model

One of the most interesting phenomena in nature is ferromagnetism. A FM material exhibits a non-zero spontaneous magnetization in the absence of an applied magnetic field. This occurs below a well-defined critical temperature T_c known as the Curie temperature. For $T > T_c$ the magnetization vanishes. Hence T_c separates two phases, a disordered one for $T > T_c$, and a ferromagnetic one for $T < T_c$.

Although the Ising model is too simple, it already contains much of the physics of the FM phase transition. In order to explore the properties of this model, we need to calculate some physical quantities of interest, including the mean energy $\langle E \rangle$, the mean magnetization $\langle M \rangle$, the heat capacity C, and the magnetic susceptibility χ.

8.4.1 The heat capacity

One way to measure the heat capacity at constant external field id from the definition:

$$C = \frac{\partial \langle E \rangle}{\partial T}.$$

Another way is to use the statistical fluctuations for the total energy in the canonical ensemble:

$$C = \frac{1}{k_B T^2} \left(\langle E^2 \rangle - \langle E \rangle^2 \right).$$

8.4.2 The magnetic susceptibility

The magnetic susceptibility χ is an example of a “response function ”, since it measures the ability of a spin to “respond” or flip with a change in the external magnetic field. The zero isothermal magnetic susceptibility is defined by the thermodynamic derivative

$$\chi = \lim_{H \to 0} \frac{\partial \langle M \rangle}{\partial H}.$$

The zero field susceptibility can be related to the magnetization fluctuations in the system:

$$\chi = \frac{1}{k_B T} \left(\langle M^2 \rangle - \langle M \rangle^2 \right),$$

where $\langle M^2 \rangle$ and $\langle M \rangle^2$ are zero field values.

8.5 Metropolis algorithm

8.5.1 Boundary conditions

As discussed earlier, the use of PBC minimizes the finite size effects. However, a disadvantage is that they reduce the minimum separation between two spins to half the length of the system.

8.5.2 Initial conditions and equilibration

We can pick a random initial configuration. However, as we shall see, in some simulations the equilibration process can account for a substantial fraction of the total computer time. The most practical choice of an initial condition is an "equilibrium" configuration of a previous run which is at a temperature close to the desired temperature.

8.5.3 Tricks

It is convenient that we store all the transition probabilities in lookup tables, so we do not have to calculate them at each step. Another trick consists of storing all the positions of the spins and their neighbors to avoid calculating many random numbers. If you need to perform several runs for different values of the temperature T, you can do it at the same time using the same random numbers.

Exercise 13.3: Equilibration of the 2D Ising model

1. Run your simulation with $L = 8$ and $T = 2$ and choose the initial spins to be all up. Plot the variation of the energy and the magnetization with time. How much time is necessary for the system to reach equilibrium?

2. Visually inspect several "equilibrium" configurations. Is the system ordered or disordered?

3. Run the program with $T = 1.5$ and chose the same initial configuration with all the spins up. How long does it take for the system to reach equilibrium?

4. Visually inspect several equilibrium configurations with $T = 1.5$. Are they more or less ordered than those in part 2?

8.6 Measuring observables

Note that after reaching equilibrium we wish to compute the mean values of several physical quantities of interest. In general this is quite time consuming and hence we do not want to calculate their values more that necessary. After a single spin flip of one spin, the values of the observables in the two configurations will not differ much, and will be almost the same. Ideally, we wish to compute the observables for configurations that are statistically independent. This means that we have to run the simulation severals steps in between measurements. This number of steps is a typical quantity that depends on the physics of the model, the parameters used, the temperature, and in particular, the "update dynamics" used in the algorithm, as we shall see below. This "correlation time" is not known *a priori*, and we have to estimate it with a preliminar test run.

One way to determine the time intervals over which configurations are correlated is to compute the time-dependent autocorrelation functions defined by:

$$C_M(t) = \langle M(t)M(0)\rangle - \langle M\rangle^2$$

and

$$C_E(t) = \langle E(t)E(0)\rangle - \langle E\rangle^2.$$

Note that at $t = 0$, C_M is proportional to the susceptibility, and C_E is proportional to the heat capacity. For sufficient large t, $M(t)$ and $M(0)$ will become uncorrelated, and

$$\langle M(t)M(0)\rangle \to \langle M(t)\rangle\langle M(0)\rangle = \langle M\rangle^2$$

, and the same will occur with C_E. Hence C_M and C_E should vanish for $t \to \infty$. In general, we expect these quantities to decay exponentially with time. The time is takes $C(t)$ to decay to $1/e$ of its value at $t = 0$ is an estimate of the autocorrelation time τ. Since configurations separated by times less that τ are statistically correlated, we will compute the desired physical quantities for times intervals of the order of τ rather than after each MC step.

Exercise 13.4: The correlation time

Consider $L = 8$ and $T = 3.0$ (high T) and $T = 2.3$, and $T = 1.5$ (low T). Estimate the correlation time τ for the energy and the magnetization fluctuations. Are the values comparable for the two fluctuations? How do your estimates for τ compare with your estimates for the relaxation time found in the previous problem?

8.6.1 Exercise 13.5: Comparison with exact results

1. Generate all the possible configurations of spins for $L = 4$.
2. Calculate the mean value of the energy, magnetization, susceptibility, and heat capacity as a function of the temperature. For calculating the magnetization use $|m|$ instead of m.
3. Use your MC program to compute the same quantities and compare with the exact results. Use the necessary MC steps to obtain an accuracy of 1% for the energy.

8.7 The Ising phase transition

We have seen that at $T = T_c$, the magnetization vanishes. This happens continuously with increasing temperature and hence, it is a "2nd order" phase transition. In 1st order phase transition the magnetization, vanishes abruptly. A way to characterize phase transition is though studying the "critical behavior" of the system. First, we have to define a quantity called "order parameter" which vanishes above the critical temperature, and is finite below it. We clearly see that the magnetization satisfies this criterion, and is a suitable candidate. The critical behavior of the system is determined by the functional form of the order parameter near the phase transition. In this region, physical quantities show a power law behavior

$$m(T) \sim (T - T_c)^{\beta},$$

where β is the "critical exponent". Although M vanishes with T, thermodynamic derivatives such as the heat capacity and sucseptibility diverge at T_c:

$$\chi \sim |T - T_c|^{-\gamma}$$

and

$$C \sim |T - T_c|^{-\alpha}.$$

We have assumed that the exponent is the same on both sides of the transition.

Another measure of the magnetic fluctuations is the linear dimension $\xi(T)$ of a typical magnetic domain. We expect that this "correlation length" to be the order of the lattice spacing for $T \gg T_c$. Since the alignment of the spins will become more correlated as T approaches T_c from above, ξ will increase. We can characterize the divergent behavior of $\xi(T)$ near T_c by a critical exponent η

$$\xi(T) \sim |T - T_c|^{-\eta}$$

A finite system cannot observe a true phase transition. Nevertheless we expect that if the correlation length is less than the linear dimension L of the system, then a finite system will be an accurate representation of the infinite system. In other words, our simulations would yield accurate results comparable to an infinite system is T is not too close to T_c.

Exercise 13.6: Qualitative behavior of the 2D Ising model

Calculate $\langle E \rangle$, C, χ and m as a function of temperature for $L = 4$, $L = 8$ and $L = 16$. Plot the results and describe their qualitative behavior. Do you see any evidence of a phase transition?

Exercise 13.7: Critical slowing down

1. Consider the 2D Ising model on a square lattice with $L = 16$. Compute the correlation time τ for $T = 1.5$, 2.4, and 2.3. Show that τ increases as the critical temperature is approached, a physical effect known as "critical slowing down".

   The magnitude of τ depend in part on our choice of "dynamics". Although we generate trial configurations attempting a single spin flip, it is possible to simultaneously flip two or more spins, even an entire cluster. This other update strategies are more efficient and lead to smaller correlation times.

9 Quantum Monte Carlo

9.1 Variational Monte Carlo

We begin our description of the Quantum Monte Carlo variants with the Variational Monte Carlo (VMC), the most transparent application of the ideas described in previous sections. This algorithm is in the borderline that divides the classical methods from the genuine quantum simulations. Although quantum in nature, it is not the action of the model that is sampled, but a trial wave function.

The main ingredient is a trial wave function $|\psi_T(\overline{\eta})\rangle$, that depends on a set of parameters $\overline{\eta}$. This wave function is represented in terms of a basis of orthogonal states $|x\rangle$

$$|\psi_T(\overline{\eta})\rangle = \sum_x \langle x|\psi_T(\overline{\eta})\rangle |x\rangle = \sum_x C_x(\overline{\eta})|x\rangle,$$

where the coefficients of the parametrization are known functions of $\overline{\eta}$. We would like the wave function to be a good representation of the actual ground state of a model. Finding the best wave function means finding the right set of parameters $\overline{\eta}$ that maximize the overlap with the actual ground state. In practice this is impossible since we do not know the groud state *a priori*, and some physical insight is needed to derive a good analytical approximation. Then we apply the variational principle, that states that the variational energy of the trial state is always greater or equal to the exact energy of the ground state:

$$\langle E\rangle_T = \frac{\langle \psi_T \mid H \mid \psi_T\rangle}{\langle \psi_T \mid \psi_T\rangle} \geq E_0, \tag{280}$$

and we use the criterium of minimizing the variational energy. In order to do that we require to calculate this quantity for different sets of parameters $\overline{\eta}$, and once we found a proper wave function, we can calculate the physical quantities of interest.

The expectation value of an arbitrary operator O is

$$\begin{aligned} \langle O\rangle_{Var} &= \frac{\langle \psi_T \mid O \mid \psi_T\rangle}{\langle \psi_T \mid \psi_T\rangle} \\ &= \frac{\sum_x \langle \psi_T \mid x\rangle\langle x \mid O \mid \psi_T\rangle}{\sum_x \langle \psi_T \mid x\rangle\langle x \mid \psi_T\rangle} \end{aligned} \tag{281}$$

$$\begin{aligned} &= \frac{\sum_x |\langle \psi_T \mid x \rangle|^2 \sum_{x'} \langle x \mid O \mid \psi_T \rangle / \langle x \mid \psi_T \rangle}{\sum_x |\langle \psi_T \mid x \rangle|^2} \\ &= \sum_x P_x O_x, \end{aligned} \tag{282}$$

with

$$P_x = \frac{|\langle \psi_T \mid x \rangle|^2}{\sum_x |\langle \psi_T \mid x \rangle|^2}, \tag{283}$$

and

$$O_x = \frac{\langle x \mid O \mid \psi_T \rangle}{\langle x \mid \psi_T \rangle}. \tag{284}$$

The equation (282) has precisely the form of a mean value in statistical mechanics, with P_x as the Boltzmann factor:

$$P_x \geq 0; \sum_x P_x = 1.$$

The first step in order to calculate it consists of generating a collection of configurations distributed according to this probability. For that purpose we employ the Metropolis algorithm: starting from a configuration $|x\rangle$, we accept a new configuration $|x'\rangle$ with probability $R = |\langle \psi_T \mid x' \rangle|^2 / |\langle \psi_T \mid x \rangle|^2$, or $1/(1+R)$ if we use the heat bath approach.

The variational simulations are simple to perform and very stable. Since the probabilities do not deppend on the statistics of the particles involved, they do not suffer from the sign problem. However, the results deppend decisively of the quality of the variational wave function, because they are completely pre-determined by it, and the physical arguments that define it. In the particular situation in which the trial function coincides with the exact ground state, the matrix elements (284) for $O = H$ are all equal to E_0 :

$$E_x = \frac{\langle x \mid H \mid \psi_T \rangle}{\langle x \mid \psi_T \rangle} = E_0.$$

This is the property called "zero variance": the more the wave function resembles the actual ground state, the more rapidly the variational enery converges with the number of iterations.

In general, the computation results more complicated, or numerically more expensive, when the number of variational parameters $\overline{\eta}$ that define the trial state is large. Thus, we always try to keep the form of the wave function simple enough and with only a few variational degrees of freedom.

9.2 World Line Monte Carlo

The Monte carlo methods extensively used in the study of classical systems cannot be directly applied to quantum systems. Suzuki[14] generalized a method previously proposed by trotter [?] and used to to demonstrate that every d-dimensional quantum spin system can be mapped onto a $(d+1)$-dimensional problem, similar to the Ising model, suggesting that the Monte Carlo method could be used on the resulting classical model. The first results of such calculations were presented by Suzuki *et al.* [?], who carried out simulations for the heisenberg model in 1D and the XY model in one and two dimensions. Employing a generalization of the method, de Raedt and Lgendijk [?] and Hirsch *et al* [?, ?] performed similar calculations for fermionic systems. Mor erecently, Reger and Young [?] and makivic and Ding [?] perfected the method for spin systems in two dimensions.

In this section we describe the World Line Monte Carlo method for quantum spin systems in one dimension.

9.2.1 Suzuki-Trotter transformation and the equivalent classical system

The Suzuki-trotter transformation is based on the following result: If A_i is a set of operators that do not necessarily commute with each other, then

$$e^{A_1+A_2+\cdots+A_p} = \lim_{m\to\infty}\left(e^{A_1/m}e^{A_2/m}\cdots e^{A_p/m}\right)^m \tag{285}$$

this equation is applicable to a quantum system with a partition function given by

$$Z = \mathrm{Tr}(e^{-\beta H}) \tag{286}$$

qith a Hamiltonian H and $\beta = 1/T$ the inverse temperature. In general H can be decomposed into a sum of terms H_i $(i = 1, 2, \cdots)$ (a process that is not necessarily uniquely defined [?, ?]), yielding

$$Z = \lim_{m\to\infty} Z^{(m)}, \tag{287}$$

with

$$Z^{(m)} = \mathrm{Tr}\left(e^{\Delta\tau H_1}e^{\Delta\tau H_2}\cdots e^{\Delta\tau H_p}\right) \tag{288}$$

The trace and limit operations have beeen interchanged, and we have defined a step in imaginary time $\Delta\tau = \beta/m$ (in the temperature axis, or Trotter direction). Introducing reslutions of the identity in some appropriate basis, the m-th approximant to the partition function can be written as:

$$Z^{(m)} = \left(\sum_{i_1,i_2,\cdots,i_p} \langle i_1|e^{\Delta\tau H_1}|i_2\rangle\langle i_2|e^{\Delta\tau H_2}|i_3\rangle\cdots\langle i_p|e^{\Delta\tau H_p}|i_1\rangle \right)^m , \tag{289}$$

where the error is of order $(\delta\tau 0^2$. Next, introducing new resolutions of the identity for each time interval we obtain:

$$\begin{aligned} Z^{(m)} \quad = & \sum_{i_1,i_2,\cdots,i_{mp}} \langle i_1|e^{\Delta\tau H_1}|i_2\rangle\langle i_2|e^{\Delta\tau H_2}|i_3\rangle\cdots\langle i_p|e^{\Delta\tau H_p}|i_{p+1}\rangle \\ & \langle i_{p+1}|e^{\Delta\tau H_1}|i_{p+2}\rangle\langle i_{p+2}|e^{\Delta\tau H_1}|i_{p+3}\rangle\cdots\langle i_{2p}|e^{\Delta\tau H_p}|i_{2p+1}\rangle\cdots \\ & \langle i_{(m-1)p+1}|e^{\Delta\tau H_1}|i_{(m-1)p+2}\rangle\langle i_{(m-1)p+2}|e^{\Delta\tau H_1}|i_{(m-1)p+3}\rangle\cdots\langle i_{mp}|e^{\Delta\tau H_p}|i_1\rangle \end{aligned} \tag{290}$$

What distinguished one approximation from another is the partition of the Hamiltonian. One select the partition in oder to simplify the evaluation of the matrix elements, avoid sign problems, and effectively implement the conservation rules associated to H. In general one uses a partition in real space in terms of local Hamiltonians $h_1, H_2, \cdots H_p$ that are composed by sums of two-site terms tthat do not overlap. In systems of $(d+1)$ dimensions (d physical plus the Trotter/time direction) with short range interactions, the Hamiltonian can be written as a sum of interaction terms between nearest neighbors in the lattice:

$$H = \sum_{i,\delta} H_{i,i+\delta}. \tag{291}$$

In (1+1) dimensions, the most natural choice corresponds to the so-called "checkerboard" decomposition, that consiusts of dividing the lattice into two sublattices, one containing the even sites, and the other one, the odd sites. As a consequence, the Hamiltonian can be broken into two pieces H_1 and H_2, each of them being the sum of two-site interactions between sites belonging to different sublattices:

$$\begin{aligned} H_1 &= \sum_{i \text{ even}} H_{i,i+1} \\ H_2 &= \sum_{i \text{ odd}} H_{i,i+1} \end{aligned} \tag{292}$$

We should notice that H_1 and H_2 are composed by terms that commute with eachother, hence:

$$\begin{aligned} e^{-\Delta\tau H_1} &= \prod_{i \text{ even}} e^{-\Delta\tau H_{i,i+1}} \\ e^{-\Delta\tau H_2} &= \prod_{i \text{ odd}} e^{-\Delta\tau H_{i,i+1}} \end{aligned} \tag{293}$$

As a result, the matrix elements can be obtained by simply solving a two-site problem, which has a very small number of degrees of freedom. In the case of the heisenberg model is is easy to see that:

$$\begin{aligned} e^{-\Delta\tau H_{i,i+1}}|--\rangle &= e^{-\Delta\tau J/4}|--\rangle \\ e^{-\Delta\tau H_{i,i+1}}|++\rangle &= e^{-\Delta\tau J/4}|++\rangle \\ e^{-\Delta\tau H_{i,i+1}}|+-\rangle &= [\cosh(\Delta\tau J/2)|+-\rangle + \sinh(\Delta\tau J/2)|-+\rangle]\, e^{\Delta\tau J/4} \\ e^{-\Delta\tau H_{i,i+1}}|-+\rangle &= [\sinh(\Delta\tau J/2)|+-\rangle + \cosh(\Delta\tau J/2)|-+\rangle]\, e^{\Delta\tau J/4} \end{aligned} \tag{294}$$

For each time interval $\Delta\tau$, the operator $e^{\Delta\tau H_1}$ is applied first, and then the operator $e^{\Delta\tau H_2}$. That gives rise to a graphic representation as the one shown in Fig.**??**, where the horizontal axis represente the spatial direction along the sites of the chain, and the vertical axis represnts the imaginary timer τ, whcih has been subdivided into $2m$ segments. The configuration of spins at time $l\Delta\tau$ correspond to a state $|i_l\rangle$ in the sum for $Z^{(m)}$. the shaded plaquettes correspond to slices of space and time in whcih the spins can interact and we shall call them "interacting plaquettes". The white plaquettes are called "non-interacting" plaquettes. The sum over the intermediate states correspond to summing over all the possible ways to distribute the spins in the spatial direction, for each interval of time. We have connected the $\uparrow$-projection of the spin with lines, that are precisely called "world-lines". In the Heisenberg model it is enough with following the trajectory of one kind of spin only, since the others are qutomatically determined. In the case of fermionic systems, onbe assigns a different color to each spin orientation.

For a given interval of time l, each matrix element for H_1 can be written as:

$$\begin{aligned} \langle i_l|e^{-\Delta\tau H_1}|i_{l+1}\rangle &= \langle i_l|e^{-\Delta\tau \prod_{i \text{ even}} H_i i,i+1}|i_l\rangle \\ &= \prod_{i \text{ even}} \langle i_l|e^{-\Delta\tau H_{i,i+1}}|i_l\rangle \\ &= \prod_{i \text{ even}} \langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle \end{aligned} \tag{295}$$

where the variables $S_{i,l}$ are of the ising type and can assume the values $\pm 1/2$. this expression can be rewritten as:

$$\begin{aligned}\langle i_l|e^{-\Delta\tau H_1}|i_{l+1}\rangle &= \exp\left\{\ln\left[\prod_{i \text{ even}} \langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle\right]\right\} \\ &= \exp\left\{\sum_{i \text{ even}} \ln\langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle\right\}. \end{aligned} \tag{296}$$

using the equivalent expression for H_2, we finally obtain

$$\begin{aligned} Z^{(m)} &= \sum_{\{i_1,i_2,\cdots,i_{2m}\}} \exp\left[\sum_{\text{sh.plq}} \ln\langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle\right] \\ &= \sum_{\{states\}} \exp\left[-\beta \sum_{\text{sh.plq}} \left(\frac{1}{\beta}\right) \ln\langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle\right] \\ &= \sum_{\{states\}} \exp\left[-\beta \sum_{\text{sh.plq}} h(i,l)\right]. \end{aligned} \tag{297}$$

In this expression we have replaced the sum over configurations of quantum spins by a sum over states of a $(1+1)$-dimensional system of Ising variables. The equation ([**?**]) respresents tha partition function of a two-dimensional Ising system with a 4-spin interaction:

$$h(i,j) = \left(\frac{1}{\beta}\right) \ln\langle s_{i,l}s_{i+1,l}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+1}s_{i+1,l+1}\rangle. \tag{298}$$

The six possible configurations of 4 spins allowed by the conservation rules are shown in Fig.[**?**]. the sum over states that satisfy the conservation rules is equivalent to summing over all the possible configurations of allowed world lines. Notice that these can be drwan parallel to the lateral sides of a plaquette, or crossing the diagonal of the shaded plaquettes, but never accross the diagonal of a white plaquette.

This graphic representation gives a simple picture about a given configuration and also offers an idea of the ground state of the system. Let us consider the partition function as the trace over eigenstates $|\alpha\rangle$,

$$Z = \sum_\alpha \langle\alpha|e^{-\beta H}|\alpha\rangle. \tag{299}$$

We can separate $e^{-\beta H}$ into $e^{-(\beta-\tau)H}e^{-\tau H}$, and insert a complete set of state in the S^z representation between the two exponentials. In the low temperature limit, and for each time slice τ we obtain

$$Z = e^{-\beta E_0} \sum_{\{S_i^z\}} |\langle s_1 s_2 \cdots s_N | \psi_0 \rangle|^2. \tag{300}$$

As a consequence, for each interval of time τ, the probability of finding a given set of spins $|s_1 s_2 \cdots s_N\rangle$ is proportional to the square of the projection of the ground-state on that configuration. This way, the world lines for large β offer a picture of the ground state of the system.

9.2.2 Monte Carlo simulation with worldlines

We would like to develop an algorithm to generate all the possible configurations of world lines, that is ergodic, and does not violate the conservation rules. The conservation of S^z implies the fololowing restrictions: if two spins are moved on a horizontal side of an interacting plaquette, they must necessarily be anti-parallel; if two spins on a lateral side participate, they can only move if they point in the same direction.

We mus generate all the possible closed loops under these considerations applying all the possible moved compatible with the torus topology. The toroidal geometry is a consequence of the preiodic boundary conditions in the space direction (to preserva translational invariance) and along the time direction (required by the trace operation). The minimum local move tthat we can make corresponds to moving two parallel spins from one side of a non-interacting plaquette, to the opposite side, as illustrated in Fig.[**?**]. Perdoming successive changes of this kind it is possible to generate all the possible configurations with a given "winding number", conserving the total value of S^z. We define "winding number" of a given configuration of worldlines in the following way: Since we are evaluating the trace with periodic boundary conditions, the system has the topology of a torus. Suppose that we start from an arbitrary site at $\tau = 0$ with spin $\uparrow$, and we follow the worldline continuously for an entire revolution along the time direction (τ grows from 0 to β, and returns to 0). If we arrive to the same site after a revolution, we say that tthe configuration has a winding number equal to zero; if we require n revolutions to return to the same site, we then say that the configuration has a winding number equal to $\pm(n-1)$, with the sign depending on the spatial direction we move with each revolution. In the majority of the cases, only configurations with winding number zero are important. Configurations with larger winding number can only be obtained with periodic boundary conditions, althoug it is clear that they do not occur with open boundary conditions.

The Monte Carlo algorithm we need to devise will consists of different possible moves. The local move, similar to the “flipping” move for the Ising model, would correspond to sweeping over all the sites of the lattice, and verifying that it is possible to move a worldline accross a white plaquette. If a white plaquette has its lower-left corner on site $9i, l)$ of the lattice, a move will only be possible if the quantity $s \equiv s_{i,l} + s_{i+1,l} - s_{i+1,l} - s_{i+1,l+1} = 2$. A possitive sign allows to move the line from left to right, while for a negative sign, from right to left. Is a move is possible, we need to calculate the transition probablity as the ratio between the matrix elements of the involved plaquettes, before, and after the move, for instance:

$$R = \frac{\langle i_{l-1}|e^{-\Delta\tau H_1}|i'_l\rangle\langle i'_l|e^{-\Delta\tau H_2}|i'_{l+1}\rangle\langle i'_{l+1}|e^{-\Delta\tau H_1}|i_l+1\rangle}{\langle i_{l-'1}|e^{-\Delta\tau H_1}|i_l\rangle\langle i_l|e^{-\Delta\tau H_2}|i_{l+1}\rangle\langle i_{l+1}|e^{-\Delta\tau H_1}|i_l+1\rangle} \tag{301}$$

with

$$\begin{aligned}
\langle i_{l-1}|e^{-\Delta\tau H_1}|i_l\rangle &= \langle s_{i,l-1}s_{i+1,l-1}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l}s_{i+1,l}\rangle \\
\langle i_l|e^{-\Delta\tau H_2}|i_{l+1}\rangle &= \langle s_{i-1,l}s_{i,l}|e^{-\Delta\tau H_{i-1,i}}|s_{i-1,l+1}s_{i,l+1}\rangle \\
&\quad\times\langle s_{i+1,l}s_{i+2,l}|e^{-\Delta\tau H_{i+1,i+2}}|s_{i+1,l+1}s_{i+2,l+1}\rangle \\
\langle i_{l+1}|e^{-\Delta\tau H_1}|i_{l+2}\rangle &= \langle s_{i,l+1}s_{i+1,l+1}|e^{-\Delta\tau H_{i,i+1}}|s_{i,l+2}s_{i+1,l+2}\rangle
\end{aligned} \tag{302}$$

and where the prime states correspond to configurations after the move. The ratio R depends on the number s, that indicates the direction of the move, and the numbers $s_{i+1,l}$ and $s_{i+1,l+2}$, that determine if the move is vertical or diagonal accross the upper and lower interacting plaquettes, and $s_{i-1,l}$ and $s_{i+2,l}$, that indicate if there is another additional world line moving accross the lateral interacting plaquettes.

Since we only take into account two possible configurations of world lines, we emply the ”thermal bath” algorithm to accept or reject new configurations. Therefore, we accept or not a new configuration with probability

$$P = \frac{R}{R+1}. \tag{303}$$

Besides the local moves, there are two other types of global moves necessary to preserve ergodicity. The first one is responsible for the fluctuations in the magnetization and is illustrated in Fig.[**?**]. We look for a straight line of spins pointing in the same direction, and we flip all of them simultaneously. This allows one to calculate values of the magnetization and the uniform susceptibility, which is generated by magnetic fluctuations of straight lines connecting configurations with different total magnetization. In studies of ground state properties, we require to simulate very low temperatures, and the magnetic fluctuations are negligible or null, and we can ignore them completely, working in the subspace restricted to zero magnetization.

The other global move extends along the spatial direction, and is shown in Fig.[**?**]. Its is responsible of connecting subspaces with different topology, that differ in the winding number. The absence of this type of moves can introduce finite size effects in small systems, but in sufficiently large lattices, they can be ignored.

9.2.3 Measurement and averaging

The algorithm described in the previous section generated a Markov chain of states, favoring the selection of configurations that contribute to the partition function with relatively large weights. Thsi process is simple a generalization of the importance sampling. If we denote the set of generated states $\{\sigma_\nu\}$ with $\nu = 1, 2 \cdots, M$, then the monte Carlos estimates for the mnean value of an observable A in a classical system will be given by

$$A \approx \frac{1}{M} \sum_{i=1}^{M} A(\sigma_\nu). \tag{304}$$

In this equation $A(\sigma_\nu)$ is the value of a function A in the state σ_ν. However, we must remember that in a classical system obtained from the Suzuki-Trotter decomposition, the variable A is dynamic, and depends on the temperature. therefore, we must average some adecuate function B associated to A, such that in reality we obtain:

$$A = \frac{1}{M} \sum_{i=1}^{M} B(\sigma_\nu). \tag{305}$$

For instance, let us consider the classical energies associated to the Heisenber Hamiltonian

$$\begin{aligned}
E_1^{(m)} = E_2^{(m)} &= \frac{\Delta\tau}{\beta} J/4 \\
E_3^{(m)} = E_4^{(m)} &= \frac{1}{\beta}(-J\Delta\tau/4 - \ln\cosh\left(\frac{\Delta\tau J}{2}\right) \\
E_5^{(m)} = E_6^{(m)} &= \frac{1}{\beta}(-J\Delta\tau/4 - \ln\sinh\left(\frac{\Delta\tau J}{2}\right) . \qquad (306)
\end{aligned}$$

The partition function for a single plaquette can written as

$$Z_{\text{plq.}}^{(m)} = \sum_j \exp\left(-\beta E_j^{(m)}\right), \qquad (307)$$

and the thermal average of the energy is finaly obtained as

$$\begin{aligned}
E_{\text{plq.}}^{(m)} &= -\frac{\partial}{\partial\beta} \ln\left(Z_{\text{plq.}}^{(m)}\right) \\
&= \frac{1}{Z_{\text{plq.}}^{(m)}} \sum_j \left[\frac{\partial}{\partial\beta}\left(\beta E_j^{(m)}\right)\right] \exp\left(-\beta E_j^{(m)}\right) \\
&= \frac{1}{Z_{\text{plq.}}^{(m)}} \sum_j F_j^{(m)} \exp\left(-\beta E_j^{(m)}\right) . \qquad (308)
\end{aligned}$$

In the last step we have defined $F_j^{(m)}$, the value of the "energy function" for the state j, such that tthe energy is the the thermodynamic average of a function F. The mean value of any observable can calculated in a similar way.

The equivalence between the quantum system and the classical counterpart is exact only in the limit of m going to infinity. In practice we work always with finite values of m (or $\delta\tau \neq 0$), which is a source of systematic error of the order $(\Delta\tau)^2$, which is in general small and under control. The error is independent of the volume for sufficiently large systems, and results porportional to the norm of the commutator $[H_1, H_2]$. For a large quantity of observables one can use the extrapolation

$$A(\Delta\tau) = A(0) + a/(\delta\tau)^2 + b/(\Delta\tau)^4 + \cdots, \qquad (309)$$

where $A(0)$ is the correct value. usually, only the lower oder temrs on the extrapolation are considered, such that we extrapolate with $1/(\Delta\tau)^2$. A possible approximation is to fix the value of $\Delta\tau$ to a very small number for all temperatures, such that the systematic error can be neglected, compared to the statistical error.

9.3 Determinantal (or Auxiliary Field) Monte Carlo

In this section, we will briefly describe an application of this general algorithm to the quantum mechanical many-body problem of interacting electrons on a lattice, working in the grand-canonical ensemble. The basic idea of this approach was presented some time ago by Blankenbecler, Scalapino and Sugar. [13]

Quantum Monte Carlo relies on the fact that d-dimensional quantum problems can be intepreted as classical problems in $(d+1)$ dimensions through Feymann's Path Integral representation. The task consists in identifying Ising-like fields that would allow us to evaluate the partition function and mean values using the same Metropolis algorithm we have used before in the equivalent classical model. Suzuki [14] was the first to apply this concepts after generalizing an idea by Trotter. [15]

Suppose we want to evaluate the expectation value of a physical observable $\hat{O}$, at some finite temperature $T = 1/\beta$. If $\hat{H}$ is the Hamiltonian of the model, this expectation value is defined as,

$$\langle \hat{O} \rangle_T = \frac{Tr(\hat{O}e^{-\beta\hat{H}})}{Tr(e^{-\beta\hat{H}})}, \tag{310}$$

where the notation is the standard. From now on, let us concentrate on the particular case of the one band Hubbard model which was defined previously. The Hamiltonian of this model, with the addition of a chemical potential, can be naturally separated into two terms as,

$$\hat{K} = -\mathrm{t} \sum_{\langle \mathbf{ij} \rangle,\sigma} (\mathrm{c}^\dagger_{\mathbf{i}\sigma}\mathrm{c}_{\mathbf{j}\sigma} + \mathrm{c}^\dagger_{\mathbf{j}\sigma}\mathrm{c}_{\mathbf{i}\sigma}) - \mu \sum_{\mathbf{i}} (\mathrm{n}_{\mathbf{i}\uparrow} + \mathrm{n}_{\mathbf{i}\downarrow}), \tag{311}$$

$$\hat{V} = \mathrm{U} \sum_{\mathbf{i}} (\mathrm{n}_{\mathbf{i}\uparrow} - \frac{1}{2})(\mathrm{n}_{\mathbf{i}\downarrow} - \frac{1}{2}). \tag{312}$$

Discretizing the inverse temperature interval as $\beta = \Delta\tau L$, where $\Delta\tau$ is a small number, and L is the total number of time slices, we can apply the well-known Trotter's formula to rewrite the partition function as,

$$Z = Tr(e^{-\Delta\tau L\hat{H}}) \sim Tr(e^{-\Delta\tau\hat{V}}e^{-\Delta\tau\hat{K}})^L, \tag{313}$$

where a systematic error of order $(\Delta\tau)^2$ has been introduced, since $[\hat{K}, \hat{V}] \neq 0$. In order to integrate out the fermionic fields the interaction term $\hat{V}$ has to be made quadratic in the fermionic creation and annihilation operators by introducing a decoupling Hubbard-Stratonovich transformation. At this stage, we can select from a wide variety of possibilities to carry out this decoupling i.e. we can choose continuous or discrete, real or complex fields, belonging to different groups. In particular, and for illustration purposes, here we use a simple transformation using a discrete "spin-like" field [16],

$$e^{-\Delta\tau \mathrm{U}(\mathrm{n}_{\mathbf{i}\uparrow}-\frac{1}{2})(\mathrm{n}_{\mathbf{i}\downarrow}-\frac{1}{2})} = \frac{e^{-\Delta\tau\mathrm{U}/4}}{2}\sum_{s_{\mathbf{i},\mathbf{l}}=\pm1} e^{-\Delta\tau s_{\mathbf{i},\mathbf{l}}\lambda(n_{\mathbf{i}\uparrow}-n_{\mathbf{i}\downarrow})}, \tag{314}$$

which is carried out at each lattice site $\mathbf{i}$, and for each temperature (or imaginary-time) slice l. The constant λ is defined through the relation $\cosh(\Delta\tau\lambda) = \exp(\Delta\tau\mathrm{U}/2)$. The transformation Eq.(314) reduces the four-fermion self-interaction of the Hubbard model to a quadratic term in the fermions coupled to the new spin-like field $s_{\mathbf{i},\mathbf{l}}$. Thus, in this formalism the interactions between electrons are mediated by the spin field. Now we can carry out the integration of the fermions. While this is conceptually straightforward, and for a finite lattice of N × N sites it gives determinants of well-defined matrices, arriving to the actual form of these matrices is somewhat involved, and beyond the scope of this review. Then, here we will simply present the result of the integration (more details can be found in Refs. [17] and [18]. The partition function can be exactly written as,

$$Z = \sum_{\{s_{\mathbf{i},\mathbf{l}}=\pm1\}} \det M^+(s) \det M^-(s), \tag{315}$$

where

$$M^\sigma = I + B^\sigma_L B^\sigma_{L-1} ... B^\sigma_1, \tag{316}$$

and

$$B^\pm_l = e^{\mp\Delta\tau\nu(l)}e^{-\Delta\tau\hat{K}}. \tag{317}$$

I is the unit matrix, and $\nu(l)_{\mathbf{ij}} = \delta_{\mathbf{ij}} s_{\mathbf{i},\mathbf{l}}$. Usually the physical observable $\hat{O}$, can be expressed in terms of Green's functions for the electrons moving in the spin field. Then, expressions similar to Eq.(315) can be derived for the numerator in Eq.(310). Once the partition function is written only in terms of the spin fields, we can use standard Monte Carlo techniques (such as Metropolis or heat bath methods) to perform a simulation of the complicated sums over $s_{\mathbf{i},\mathbf{l}}$ that remain to be done. The probability distribution of a given spin configuration is given in principle by $\frac{1}{Z} \det M^+ \det M^-$ (unless it becomes negative, see next section).

9.4 Projector Monte Carlo

A simple modification of the Blankenbecler, Scalapino and Sugar algorithm allows the calculation of ground state properties in the canonical ensemble i.e. with a fixed number of electrons. This approach is called "Projector Monte Carlo." Consider the ground state $|\psi_0\rangle$ of a system, and let us denote by $|\phi\rangle$ a trial state with a nonzero overlap with the actual ground state. If we apply the operator $P = e^{-\tau H}$a number m of times over an arbitrary state $|\phi\rangle$, and we intercalate the identity operator in the basis $|\alpha\rangle$ of eigenstates of H, we obtain:

$$\begin{aligned} |\phi^m\rangle &= P^m|\phi\rangle \\ &= \sum_\alpha e^{-m\tau H}|\alpha\rangle\langle\alpha|\phi\rangle \\ &= \sum_a \left(e^{-\tau E_\alpha}\right)^m |\alpha\rangle\langle\alpha|\phi\rangle \\ &= e^{-\beta E_0} \sum_a \left(e^{-\tau(E_\alpha - E_0)}\right)^m |\alpha\rangle\langle\alpha|\phi\rangle. \end{aligned} \tag{318}$$

In the limit with $\beta \to \infty$, the projection will filter out all the states with high energy and only the ground state will survive, i.e.

$$\lim_{m\to\infty} P^m|\phi\rangle = | \psi_0\rangle, \tag{319}$$

Thus, the ground state energy will be given by:

$$E_0 = \frac{\langle\phi|H|\psi_0\rangle}{\langle\phi|\psi_0\rangle} = \lim_{m,m'\to\infty} \frac{\langle\phi|He^{-m\tau H}|\phi\rangle}{\langle\phi|e^{-m\tau H}|\phi\rangle}, \tag{320}$$

while for any othe physical observable $\hat{O}$, the expectation value can be exactly written as:

$$\frac{\langle\psi_0|\hat{O}|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} = \lim_{m,m'\to\infty} \frac{\langle\phi|e^{-m'\tau H}\hat{O}e^{-m\tau H}|\phi\rangle}{\langle\phi|e^{-(m'+m)\tau H}|\phi\rangle} \tag{321}$$

This suggests that in principle, we can calculate the coeficients of the ground state of the system. However, we have to keep in mind that the dimension of the basis grows exponentially with the size of the lattice, and this will prevent us to keep in memory all the possible configurations. (Unless the system is small. Exercise for the reader: Heisenberg model on a chain with $N = 4$).

The steps necessary to Monte Carlo simulate Eq.(321) are very similar to those discussed before in deriving Eq.(315). First, the imaginary time axis is discretized in a finite number of slices, then the Trotter approximation, as well as the Hubbard-Stratonovich decoupling are used. Fermions are integrated out, and all observables are finally expressed in terms of the spin-fields which are treated using a Metropolis algorithm (for details see Ref.[18]).

Another approach that uses the same principle consists in sampling the the ground state stochastically using a set of "random walkers" $\{(w_i, |x_i\rangle)\}$, where w_i is a weight defined real and positive, and $|x_i\rangle$ are configurations usually in the S^z or occupation number representations. The objective is to obtain a distribution of weights ans states that correspond to that of the actual ground state, generating a Markov chain applying stochastically the operator P

$$(w'_i, |x'_i\rangle) \rightarrow P(w_i, |x_i\rangle). \tag{322}$$

The Projector Monte Carlo has been perfected over time, and the widely used scheme consists in using the projector operator:

$$G = [1 - \tau(H - \omega)]. \tag{323}$$

The quantity ω represents a good approximation of the ground state energy, and τ is a small time step that satisfies the condition $\tau \leq 2/(E_{\max} - \omega)$, where $E_{\max}$ is the maximum eigenvalue of H. This variant is called Green Function Monte Carlo (GFMC). (See Refs. [4]-[7] and references therein)

In practice, several walkers are used simultaneously, with the first generation of walkers $\{|x_i^0\rangle\}$ obtained using Variational Monte Carlo. This variational state is also used in the bias control and as guiding function for the importance sampling. The better the variational function, the lower the fluctuations in the mean values and the smaller the variance in the simulation. Both topics are out of the scope of this book, and the reader can find more information in the bibliography.

9.5 Sign problem revisited

For the one band Hubbard model, the Determinantal Monte Carlo simulations described before can be carried out at half-filling without problems since the product $\det M^+ \det M^-$ in Eq.(315) is positive (it can be shown that $\det M^+ = A \times \det M^-$ for any configuration of the Hubbard-Stratonovich spin fields, where A is a positive number [16]). However, in the case of an arbitrary density $\langle n \rangle \neq 1$ this is no longer true for the repulsive Hubbard model (other models like the attractive Hubbard model can still be simulated at all densities). Then, the "probability" of a given spin configuration is no longer positive definite. In this situation, to obtain results using this technique it is convenient to separate the product of the determinants into its absolute value and its sign i.e. $\det M^+ \det M^- = sign \times |\det M^+ \det M^-|$ for each spin configuration. Using this trick, the expectation value of any operator $\hat{O}$ can be written as

$$\langle \hat{O} \rangle = \frac{\langle\langle \hat{O} sign \rangle\rangle}{\langle\langle sign \rangle\rangle}, \tag{324}$$

where $\langle\langle ... \rangle\rangle$ denotes an expectation value obtained using a probability proportional to $|\det M^+ \det M^-|$. Similar tricks can be applied to cases where the determinant becomes complex as it occurs in problems of lattice gauge theory in the context of particle physics [19]. Although Eq.(324) is an exact identity, in practice the denominator can become very small if the number of spin configurations with positive and negative determinants are similar. Regretfully, this is the case for the Hubbard model in some regime of couplings and densities, and at low temperatures: the sign decreases rapidly when the temperature is reduced, specially at densities close to half-filling[18]. Actually, it has been shown that $\langle\langle sign \rangle\rangle$ converges exponentially to zero as the temperature decreases [20]. This effect imposes severe constraints on the temperatures that can be reached using Monte Carlo techniques in simulations of the Hubbard model away from half-filling.

The study of the "sign-problem", and the possibility of finding a cure for this malice, is a very important subject in the context of simulations of correlated electrons. Some time ago, considerable excitement was generated by a paper by Sorella et al. [21] where it was claimed that using a projector Monte Carlo algorithm, and an appropriate trial wave function $|\phi_0\rangle$, the mean value of the sign converges to a nonzero constant as $\beta \to \infty$. In such a case it was argued that some physical quantities could be calculated simply by neglecting the signs of the determinants. Regretfully, these conclusions were somewhat premature as discussed later by Loh et al. [20], where it was shown that the expectation value of the sign actually decreases exponentially with β. Then, neglecting the signs of the determinants leads to an uncontrolled approximation. Loh et al. [20] showed that some physical quantities related with superconducting correlations present a *qualitatively* different behavior with and without the signs included in the averages.

It is also important to clarify that the "sign-problem" is not only caused by the sign that appear due to fermionic anticommutations. For example, consider the case of spin-1/2 problems with nearest and next-nearest neighbors interactions, which can be simulated using Random Walk Monte Carlo methods [22]. In this technique, matrix elements of the interactions are used as probability in the Monte Carlo algorithm. Regretfully, it is not possible to write these matrix elements in a positive definite way for an arbitrary value of the couplings in the Hamiltonian.

Several techniques have been proposed to alleviate the sign-problem. One method is based on the possibility that the operators used to describe, e.g., hole excitations in Hubbard and $\mathrm{t-J}$ models are "poor", in the sense that they are a bad approximation to the actual "dressed" quasiparticle operators that create real holes in these models. Having proper quasiparticle operators alleviates the sign problem since in Projector or Green's function Monte Carlo methods an initial state is selected upon which $e^{-\Delta\tau\hat{H}}$ acts repeatedly till convergence is reached ($\Delta\tau$ being a small number), and thus if the initial Ansatz is very good, it may occur that the sign problem destroys the statistics only after a good convergence is observed (at least in the ground state energy). A method to systematically construct better operators was discussed by Dagotto and Schrieffer [32], Boninsegni and Manousakis [33], and Furukawa and Imada [34], with good results for the cases of one and two holes in the t − J model, and the weak coupling Hubbard model. In this technique the information gathered using Lanczos methods is very useful to guide the construction of the variational states.

The Fixed Node Monte Carlo [23] is a GFMC variant that restricts the random walkers to move into regions of the phase space in such a way that they cannot cross nodal boundaries of the wave function, where its sign changes. The nodes are provided by a suitable variational trial state. Although this method has represented a remarkable improvement in controlling the sign, the obtained results keep being variational in nature due to the constrain imposed.

A recent attemp to overcome this "stigma" in the study of strongly correlated electron models have had some notorious success in the case of frustrated antiferromagnets [24, 25], and the t-J model [26]. Instead of constraining the region where the walkers can move, this new original approach consists in performing a "stochastic reconfiguration" of the distribution of random walkers at regular intervals of the simulation, mapping them stochastically into new ones that correct the sign instabilities.

Then, the sign-problem is a widely extended plague that affects several areas of theoretical physics, not only strongly correlated electrons. The study of the sign-problem continues attracting considerable attention. Other attempts to fight it can be found in [27], [28], [29], [30], [31], [35]; and references therein.

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