

Computing Methods for Physics Condensed Matter

Final Exam, January 24th 2024

The Final Exam of the Computing Methods for Physics Course consists of two parts, corresponding to the two main topics of the course: Quantum Monte Carlo (Part I) and Density Functional Theory (DFT). You have in total four hours to solve the assignment; if you would like to hand in only one of the two parts, you will have 2 hours. You can consult any books, notes and internet websites, but communicating with other students by any means is strictly forbidden (your test will be invalidated in that case). At the end of your allotted time, please send your report as a single pdf file called "NAME_SURNAME.pdf" containing text and figures as an email attachment to: lilia.boeri@uniroma1.it and saveriomoroni@gmail.com. The email should have the subject "Computing Methods for Physics Final Exam - NAME_SURNAME" and contain as a separate attachment a zipped archive containing all input and output files required by the exercise. **Please remove unnecessary large scratch files!** Please note that NAME SURNAME indicate YOUR name and surname, respectively.

1 PART I: Quantum Monte Carlo: Crystallization of ^4He in 2D with Variational and Diffusion Monte Carlo

Helium is the only substance in Nature that remains liquid at $T = 0$ K. It crystallizes only under pressure. To high accuracy, ^4He atoms can be considered as point-like particles with zero spin, interacting through a Lennard-Jones (LJ) potential,

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (1)$$

with $\epsilon = 10.22$ K and $\sigma = 2.556$ Å (we use energy units of Kelvin and length units of Angstrom).

We will use the code `lj.f` to study ^4He in 2D near the crystallization transition at $T = 0$ with the VMC and DMC algorithms.

Our trial function will be of the Jastrow form with two- and three-body correlations,

$$\Psi_L(R) = e^{-\sum_{i < j} u_L(r_{ij})} e^{-\sum_i \sum_{j \neq i} \xi(r_{ij}) \mathbf{r}_{ij} \cdot \sum_{k \neq i} \xi(r_{ik}) \mathbf{r}_{ik}} \quad (2)$$

to describe the liquid phase, and a "Nosanow" function

$$\Psi_S(R) = e^{-\sum_{i < j} u_S(r_{ij})} e^{-\sum_i |\mathbf{r}_i - \mathbf{s}_i|^2 / d^2} \quad (3)$$

to describe the solid. In the Nosanow function there are two-body correlations and a gaussian factor localizing the i th particle within a distance $\sim d$ around a preassigned lattice site \mathbf{s}_i . This trial function breaks the Bose symmetry because each particle is identified by its lattice site. However since particle exchanges are rare in the solid this is a good approximation.

Files:

- `doc_lj.pdf`: this file
- `setup_lj.f`: a setup fortran code

- **lj.f**: the QMC fortran code¹
- **lj.h**: a file included by **lj.f** at compile time
- **statfor.f**: fortran code for statistical analysis (see Appendix C)
- **statforw.f**: same as **statfor.f** for weighted averages (see Appendix D)

¹This is essentially the same code used for the electron gas in the lab and in the first test.

Assignments

For each question, write the answer on a text file and keep a copy of the output files. At the end of the test, compress the folder(s) with your work and send it by email to saveriomoroni@gmail.com.

Part A. General questions (10 points out of 30)

1. Why do we use correlated wave functions such as (2) and (3)?
2. Why do we use Monte Carlo to calculate expectation values with wave functions such as (2) and (3)?
3. How do we choose the time step (size of the move) in VMC?
4. Does the average energy depend on the time step in VMC?
5. How do we choose the time step and the trial energy in DMC?
6. Does the average energy depend on the time step in DMC?
7. Why do we need a population of walkers in DMC?
8. Does the average energy depend on the number of walkers in DMC?
9. For a potential which diverges at zero distance, do spin-1/2 fermions have a different cusp condition in the Jastrow factor for parallel or antiparallel spins?
10. Does the cusp condition apply to bosons? If the parallel and antiparallel fermion cusp conditions are different, which one applies to bosons?

Part B. Simulations (20 points out of 30)

Compile all four codes `setup_lj.f`, `lj.f`, `statfor.f`, `statforw.f`. With the `gfortran` compiler, use the options `-w` to suppress warning messages, `-O3` to get a faster executable, `-o filename` to choose the name of the executable, and `-fallow-argument-mismatch` if you get argument mismatch errors.

The setup code prompts you to choose the run id (the name of the simulation), the density ρ , and the phase (Jastrow wave function for the liquid or Nosanow wave function for the solid). It produces all needed files, with wave functions already optimized, and a file `runid` which contains the chosen run id (the QMC code `lj.f` will run the simulation specified in the file `runid`).

You have to create the input file `xxx.in`, where `xxx` is your chosen run id. See Appendix B for the keywords of the input file.

1. In 2D, ${}^4\text{He}$ is expected to crystallize at a density ρ of about 0.07\AA^{-2} . At this density, run a VMC simulation for the liquid and one for the solid (use a different run id for the two cases). Remember to choose an appropriate time step. In at least one case, use the `statfor.f` code to check for possible autocorrelation. In the output files, the entry `e2` is the average of the square of the local energy. Use `e2` and `elocal` to calculate the variance of the local energy for the liquid and for the solid. Based on these variances, which phase is described more accurately by the wave functions generated by the setup?
2. Change the density, increasing and decreasing in steps of $\sim 0.01\text{\AA}^{-2}$, and run a few more VMC simulations to locate the crystallization density (just a rough estimate: a careful calculation, not requested here, would need a Maxwell double-tangent construction on the equation of state $E(1/\rho)$ to locate the coexistence region between the melting and the freezing densities).
3. For $\rho = 0.07\text{\AA}^{-2}$, run a DMC simulation for the liquid and one for the solid phase. Remember to generate the initial population with VMC (50 walkers is OK) and to choose an appropriate time step and trial energy. In at least one case, use the `statforw.f` code to check for possible autocorrelation. Would a DMC calculation shift the crystallization to lower or higher density? For each of the two phases, compare the VMC and DMC energies: how does this comparison relate with the variance of the local energy (question B1)?

Appendix A: Keywords for the file `xxx.sy` used in this calculation

ndim d

d (integer): dimensions of the physical space

type name number hbs2m file

define a type of particles

name (string): name of this type of particles

number (integer): number of particles of this type

hbs2m (real): value of $\hbar^2/2m$ for this type of particles

file (string): file with initial configuration(s) of the particles

v2 name_a name_b file iexp

pair potential between particles of type **name_a** and **name_b**

name_a (string): name of a type of particles

name_b (string): name of a type of particles

file (string): name of the file with the tabulated potential

iexp (integer): the short-range part of the tabulated potential is multiplied by a factor $r^{-\text{iexp}}$

u2 name_a name_b file

two-body Jastrow factor for particles of type **name_a** and **name_b**

name_a (string): name of a type of particles

name_b (string): name of a type of particles

file (string): name of the file with the tabulated Jastrow factor

vshift value

value (real): a constant shift in the potential ²

vtail value

value (real): a tail correction in the potential energy

pbc L_x [L_y [...]]

periodic boundary conditions

L_x (real): side of the simulation cell in the *x* direction

[...] (real): side of the simulation cell in the other direction(s)

u3 name_a name_b file

three-body Jastrow factor for particles of type **name_a** and **name_b**

name_a (string): name of a type of particles

name_b (string): name of a type of particles

²The LJ potential $v(r)$ is shifted to zero at $r = L/2$, and taken to be zero for larger distances; **vshift** puts back the shift in the average potential energy, and **vtail** puts back, approximately, the effect of the potential for $r > L/2$.

file (string): name of the file with the tabulated three-body function

sites name number file

define a set of lattice sites

name (string): name of the lattice sites

number (integer): number of sites

file (string): name of the file with the lattice sites' positions

nosanow name_a name_b file

nosanow function for particles **name_a** and sites **name_b**

name_a (string): name of the particles

name_b (string): name of the sites

file (string): name of the file with the tabulated nosanow function

gofr

turn on the calculation of the pair distribution function

sofk

turn on the calculation of the $S(\mathbf{k})$ for $\mathbf{k}_n = (0, n \frac{2\pi}{L_y})$

Appendix B: Keywords for the file `xxx.in` used in this calculation

```
vmc nblocks nstep tstep [istore]  
    define a VMC run  
    nblocks (integer): number of blocks  
    nsteps (integer): number of steps per block  
    tstep (real): time step (size of the move)  
    istore (integer, optional): store a configuration every istore step  
dmc nblocks nstep tstep nwalkers etrial  
    define a DMC run  
    nblocks (integer): number of blocks  
    nsteps (integer): number of steps per block  
    tstep (real): time step  
    nwalkers (integer): number of walkers  
    etrial (real): initial value of the trial energy
```

Appendix C: Statistical analysis using the code **statfor.f**

compile the code, e.g. `gfortran statfor.f -o statfor.x`

the code reads a stream of numbers from standard input

writes number of data, mean, variance, correlation time, number of independent data and statistical error on standard output

also writes: a 51-bin histogram of data on file 'histo.out', and the autocorrelation of the data on file 'corr.out'

to analyze (say) the block averages of elocal from file `vmc.out`, use the command:

```
grep elocal vmc.out | ./statfor.x
```

Appendix D: Statistical analysis using the code **statforw.f**

compile the code, e.g. `gfortran statforw.f -o statforw.x`

the code reads two streams of numbers (data and weights) from standard input

writes number of effective data in the weighted average, mean, variance, correlation time, number of independent data and statistical error on standard output

also writes: a 51-bin histogram of data on file 'histo.out', and the autocorrelation of the weighted data on file 'corr.out'

to analyze (say) the block averages of elocal from file `dmc.out`, use the command:

```
grep elocal dmc.out | awk '{print $1, $4}' | ./statforw.x
```

References

- [1] Y. Kwon, D.M. Ceperley, and R.M. Marin, Phys. Rev. B **48**, 12037 (1993)

2 PART II: Density Functional Theory

Magnesium diboride (MgB_2), discovered in 2001, is currently the record-holder conventional superconductors; its relatively high critical temperature (T_c) and ease of manufacturing make it one of the most promising materials for large-scale superconducting applications. The crystal structure of MgB_2 , shown in Fig. 1(a), comprises hexagonal graphite-like boron planes intercalated by Mg atoms. The band structure, shown in Fig. 1(b) is relatively simple, and bears a strong resemblance to that of graphite; the Fermi level cuts the electronic structure in the region close to the top of the σ band, creating a characteristic Fermi surface with disjoint σ (blue) (small tubes around the Γ point) and π (tubes around the zone boundaries) sheets – Fig. 1(c). Soon after the MgB_2 discovery several theoretical papers studied the electronic properties of related diborides, with chemical formula XB_2 , in the hope of identifying other, possibly improved, superconductors. More than twenty years later, MgB_2 properties remain however unmatched. In this test, you will study the electronic properties of these hypothetical compounds.

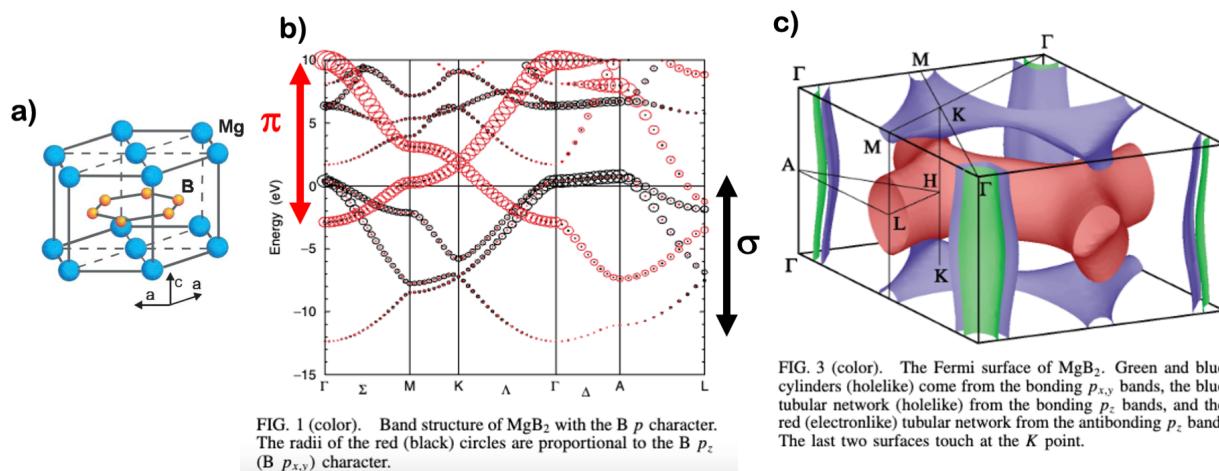


Figura 1: Crystal and electronic Structure of Magnesium Diboride (MgB_2).

► Preliminary Steps:

- Download and unzip the archive `psp_forexam.tar.gz` from the e-learning website of the course. The archive contains GGA Norm-Conserving pseudopotentials from the Pseudo-dojo website for selected elements of the periodic table.
- Each student has been assigned a different *student number*. Consult the table – Fig. 2 – to see which element X corresponds to your number. This defines a different diboride XB_2 (a diboride), for which you should perform calculations as described in the text. For example, according to the table, the student number 8 should consider the TiB_2 compound.

► Initial Structure Setup and Convergence of the Relevant Input Parameters:

The crystal structure of MgB_2 is defined by the following structural parameters:

Space group (Bravais Lattice): 191 (h).

Lattice Parameter: $a=3.083 \text{ \AA}$, $c=3.521 \text{ \AA}$.

Atomic coordinates (Wyckoff Positions): Mg (1a); B (2d).

1. Setup an initial input file for quantum `espresso` calculation for the diboride XB_2 , using the same structural parameters as MgB_2 . The file should contain all parameters needed to run a standard self-consistent calculation. Answer the following questions:

How many valence, core and total electrons are there in your system? Is this number higher or lower than that you would expect in MgB₂? (If needed, the Mg pseudopotential is included in the `psp_forexam.tar.gz` archive).

2. Once you have verified that your input file is correctly set up, run all convergence tests required to attain an accuracy on the total energy of at least 10 meV/atom. Produce a separate plot for each convergence test, with a short explanation (max 50 words for each plot).
3. Analyze the forces and the stress tensor of your hypothetical XB₂ structure and answer the following questions:
 - What is the general definition of the forces and stress tensor? How are they computed in `quantum espresso`? (max 100 words)
 - What are the forces acting on the atoms in your system? Why? Look at the stress tensor: is it isotropic or anisotropic? What does it mean? What do you expect will happen if you perform a structural relaxation? (max 100 words)

► **Structural Relaxation and Electronic Structure:** In the second part of the exercise you will relax the XB₂ to its ground-state structure, and study its electronic properties.

1. Relax the XB₂ structure to its ground-state (zero pressure) structure. Answer the following questions: What is the new volume of the unit cell? What is the new *c/a* ratio? Are these values larger or smaller than in MgB₂? What is the interatomic in-plane B-B distance? What is the out-of-plane B-B distance?
2. Compute the electronic structure along high-symmetry directions in the BZ and the corresponding Density of States (DOS) for XB₂ at ambient pressure.
3. Compare your bands to those of MgB₂ in Fig.- 1. Answer the following questions:
Can you identify the σ and π bands in your plot? What types of electronic states form your Fermi surface?
Can you understand your results based on the number of valence electrons in your system? (Max 200 words)

► **Appendix: Group/Element table:**

Group	Element	Group	Element
1	Li	9	V
2	Be	10	Cu
3	Na	11	Zn
4	Al	12	P
5	K	13	S
6	Ca	14	Cl
7	Sc	15	Rb
8	Ti	16	Sr

Figura 2: Group/Element Correspondence.