Overview Lecture Notes

1   Goals

In practice, the goal of this course is to enable the student to apply density functional theory (DFT) to complex materials, and properly interpret the results. This sounds both simple and complicated, and it is. The availability of both commercial/open-source DFT codes and cheap computers removes the huge barrier for non-experts to perform calculations. HOWEVER, this does not remove the possibility of people doing horrible research and misusing/abusing methods. A strong effort in this course should allow a student to do publishable research using DFT. The student should be able to compile a code and run in serial or parallel. Ultimately, one should be able to predict the properties of materials!

2   Perspective on the many-body problem

The goals of science are pretty simple: understand, predict, and manipulate the behavior of nature. Of course, our interests in nature regards materials. Humanity made great progress understanding nature since prehistory, carefully deducing the character of our surroundings and harnessing our surroundings by developing tools. However, the ability of humanity to predict the behavior of nature remained limited and empirical at best until modern times. That largely changed with Isaac Newton and the advent of classical mechanics. Newton published his three laws of motion in Principia on 5 July 1687. At this point, we knew the laws of motion and could predict the motion of a macroscopic object subject to some external force. At this time, the only force we had a decent understanding of was gravity, which Newton also addressed in his Principia. Nonetheless, much of the necessary formalism was present to understand the basics of planetary motion. The difficulty of the many-body problem (ie. solving the equations with many interacting objects present) was probably immediately apparent. It was not long after that people were already applying Newtons Laws based on the speculation of the existence of atoms. For example, Bernoulli published his *Hydrodynamica* in 1738, where he laid the groundwork for the kinetic theory of gasses assuming the existence of atoms.

About one hundred years after Newtons revelation, in 1785, Coulomb presented his work on electricity which deduced the nature of the of the force between electric charges (ie. Coulombs law).

In 1814, Laplace made a fascinating statement which demonstrated his understanding of the implications of what was known.

We may regard the present state of the universe as the effect of its past and the cause of its future. An intellect which at a certain moment would know all forces that set nature in motion, and all positions of all items of which nature is composed, if this intellect were also vast enough to submit these data to analysis, it would embrace in

a single formula the movements of the greatest bodies of the universe and those of the tiniest atom; for such an intellect nothing would be uncertain and the future just like the past would be present before its eyes. Laplace - 1814

In essence, Laplace is lamenting the difficulty of solving the classical many-body problem. He alludes that if one could solve it, we would have complete predictive power. Of course, Laplace did not know about quantum mechanics, nor about chaos, but nobody is perfect! Another fascinating aspect of this quote is Laplace's reference to "this intellect", which is now known as a computer! Of course, if one ignored the interaction between the "tiniest atom" one would have many one-body problems instead of one many-body problem, and then some progress could be made even at this time. This was already long accomplished by Bernoulli in 1738.

Laplace's foreshadowing is currently a vibrant area of research which goes under the name of molecular dynamics. Classical force fields which describe the energy of a material as a function of atomic displacement are guessed or fit to experiment. Then the classical equations are solved by brute force, and one can treat millions/billions of atoms depending on the timescales and algorithms being considered. This is NOT what we are doing in this course.

In 1892, Lorentz polished off the work of Maxwell (ie. 1873) by characterizing the force exerted on a mobile electric charge in a magnetic field. At this point, we knew all the relevant forces necessary to study essentially all chemical and biological processes.

In 1897, JJ Thompson discovers the electron. In 1900 Drude boldly neglected Coulomb interactions and applied the kinetic theory of gases to the electron gas.

Around 1925-1926 the laws changed! Schrodinger published his famous wave equation, Heisenberg published his matrix mechanics, and Dirac showed them all up with his canonical quantization. New laws of physics were born and hence a new many-body problem was born: the quantum many-body problem. After this, things happened extremely rapidly. In 1926 Pauli solved the Hydrogen atom, and he also discovered the exclusion principle.

By 1929, the implications of their present state of knowledge was entirely clear, as indicated by this quote from Dirac:

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Proc. Royal Soc. London Vol. 123 (1929)

Nobel prize winner Walter Kohn summarized it well: *In general the many-electron wave function $\Psi(r_1, ..., r_N)$ for a system of N electrons is not a legitimate scientific concept, when $N > N_0$, where $N_0 \approx 10^3$.* - RMP v71 (1999).

Even if divine being told you the many-electron wave function, you could not write it down! The complete soln of QMBP is not tractable for large systems... and it likely never will be. Of course, this is a bit of a straw man, because the many-electron wavefunction contains much more information than we could ever care to know. In reality, all we want to know are certain expectation values of operators, and the result

of this is easy to write down. Nonetheless, we still need approximations to accomplish this.

At this point, the physics of condensed matter had two major problems.

1. How does one deal with the electron-electron interactions. This is a many-body problem, and we are going to focus on techniques which map this many-body problem to an effective one-body problem.

2. How does one deal with the periodic array of nuclear potentials in a solid material. This is a one-body problem but it is still hard!

In order to make progress on solving the many-body schrodinger equation for molecules and solids, it was clear that some approximations would be needed. The first question was addressed by the work of Hartree in 1928. It is assumed that the many-particle wavefunction can be approximated as a product of single particle wavefunctions, and the expectation value of the Hamiltonian is minimized under the constraint that the single-particle wavefunctions are orthonormal. This results in a set of *single-particle* equations, where the effects of the electron-electron interactions have been effectively lumped into the single-particle potential. This is a sort of mean-field theory, and the spirit of this approach carries with us to this day.

In 1929 Slater and V. A. Fock independently extended Hartree's method by including the antisymmetry of the wavefunction, giving rise to the so-called Hartree-Fock equations. Once again, this results in a set of effective *single-particle* equations, where the single particle potential now has an additional term beyond Hartree (ie. the exchange term). The Hartree-Fock equations are still in use to this day.

Regarding question 2, some progress was made by Bloch in 1928 with the derivation of Bloch's theorem. Thereafter, one could treat the effect of a weak periodic potential via perturbation theory, demonstrating the splitting of bands at the Brillioun zone boundary (ie. nearly-free electron model).

In 1933, Wigner and Seitz made some progress on treating question 2 with their introduction of the cellular method. The essence of the cellular method is to partition the solid into a set of space-filling Wigner-Seitz cells. The Schrodinger equation within the cell is then solved, subject to the condition that the wavefunction must be continuous and differentiable. This is a crude approach and is no longer used.

In 1937, Slater introduced his Augmented plane-wave method. In this approach, one starts by introducing the concept of a "muffin-tin" potential. One constructs non-space-filling spheres around each nucleus, and the potential is supposed to be the nuclear potential within the sphere and a constant outside the sphere. Basis functions are then constructed by solving the Schrodinger equation within the sphere, and then matching this solution on the sphere boundary to a plane wave. Hence the name, augmented plane wave. These are then used as a basis to diagonalize the Hamiltonian. This approach is the precursor to probably the most accurate basis set in use today: the linearized augmented plane wave method (LAPW). See more below.

In 1940 Herring introduced a very different approach, the so-called orthogonalized plane wave method. The essence of his idea was to construct basis functions which were plane waves that had been orthogonalized to the deeply bound core electrons. This idea

was the precursor to the pseudopotential, which plays a prominent role in electronic structure calculations.

In 1947 Korringa and in 1954 Kohn and Rostoker developed the KKR method. This a Greens function approach to Slater's muffin-tin potential.

In 1959, Antoncik and independently Phillips and Kleinman introduced the concept of the pseudopotential. This amounts to replacing the nuclear potential with an effective, weaker potential such that ordinary plane waves can be used as a basis set.

In 1964 a major breakthrough occurred with respect to treating the electron-electron interactions. Pierre Hohenberg and Walter Kohn determined that there exists an energy functional of the density which delivers the ground state energy and density at its global minimum. This was the birth of modern density functional theory (DFT). In 1965, Walter Kohn and Lu Sham took this idea of DFT, which was still somewhat academic, and wrote down the Kohn-Sham equations and the so-called local density approximation (LDA). This was a enormous advancement, for which Kohn was awardwed the 1998 Nobel prize in chemistry. As you may know, DFT within LDA is still wildly popular to this day. Furthermore, it is probably fair to say that very few appreciable advancements have been made to DFT since its inception.

In 1971, Ole Andersen developed the Muffin-tin orbital method. This is similar in spirit to Slaters APW method in that you are matching an atomic-like solution within a sphere to some other function in the interstitial. However, the essence of this approach was to be minimal, and hence require only a few basis functions for expanding the wavefunction.

In 1973, Ole Andersen made a very important step. He "linearized" both the APW method of Slater in addition to his MTO method. This gave birth to the so-called LAPW method and the LTMO methods, and slight variants of these techniques are two of the most prominent basis sets in use today.

In 1990, Vanderbilt finished the story of the pseudopotential with his ultra-soft pseudopotentials. While in 1994, Blochl introduced the idea of Projector Augmented Waves (PAW). This can be viewed as a unification of LAPW and ultrasoft pseudopotentials.

In conclusion of the story of basis sets for treating the one electron potential, there is no clear winner as different techniques have different advantages and disadvantages. LAPW is usually touted as the most accurate basis set, although this is usually not a huge concern. Planewaves and Pseudopotentials are probably the most computationally favorable (aside from linear scaling methods) and are most conducive for computing forces and hence doing first-principles molecular dynamics. LMTO probably gives the most insight into the result given their minimal nature. However, these statements are somewhat open to debate! What is not open for debate is that all of these are still used appreciably. Also, there are a few others which I have left out.

Of course, one could not leave out a comment about the role of computers in this development. All of these approaches are a bit different, but all require numerical computation. Computations using Hartree-Fock and the APW method and primitive computers were beginning to appear in the late 1950's and early 1960's. One can look at the early work by Wood, who was a research scientist in Slater's group at MIT (Phys.

Rev. 126, 517 (1962)), where he calculated the energy bands of iron.

Moreover, the method is one which is quite adaptable to a digital computer and has been programmed for the Whirlwind computer (by Saffren) and for the IBM 704 and 709 computers.

From wikipedia:

The Whirlwind computer was developed at the Massachusetts Institute of Technology. It is the first computer that operated in real time, used video displays for output, and the first that was not simply an electronic replacement of older mechanical systems. Its development led directly to the United States Air Force's Semi Automatic Ground Environment (SAGE) system, and indirectly to almost all business computers and mini-computers in the 1960s. Whirlwind I ran in a support role for SAGE until June 30, 1959. A member of the project team, Bill Wolf, then rented the machine for a dollar a year until 1973. Ken Olsen and Robert Everett then saved the machine from the scrap heap and it became the basis for the Digital Computer Museum, which would later become The Computer Museum on Boston's Museum Wharf. Today it is in the collection of the Computer History Museum in Mountain View, California, and a portion of the machine is currently on display.

Of course, this calculation can now be trivially done on any laptop.

So what is the state of the art now? Using Pseudopotential and plane waves, one can handle systems with unit cells containing on the order of 1000 atoms. DFT usually scales something like the number of atoms to the square or the cube depending on the basis set. However, there are linear scaling DFT techniques which may be able to reach an order of magnitude higher in the number of atoms. DFT is currently being applied to nearly anything you can think of, ranging from the usual metal alloys to DNA to nanoparticles.

The beauty of Kohn-Sham DFT within LDA is that it provides us with an effective single-particle equation which can relatively easily be applied to any atom, molecule, or material. HOWEVER, one must never forget that you are using an approximation and that this does have limitations. In particular, DFT has not yet been effectively implemented at appreciable temperatures, although in principle there are no limitations. Additionally, DFT is a ground state theory, so it does not tell you about the excited state properties. Finally, DFT within all known implementations does qualitatively fail in systems where the electrons are strongly correlated. Mott proposed that when the electron interactions overwhelm the band energy, the electrons will localize and the system will become an insulator. This is indeed realized experimentally in certain materials, and DFT within all known implementations will predict a metal. A strongly correlated electron system is a system which is "near" a Mott insulator, in some measure which is not precisely defined. Perhaps the most famous example of a strongly correlated electron system is the copper oxide superconductors, which conduct electricity with zero resistance at temperatures above that of liquid nitrogen. The Nobel prize was awarded to Bednorz and Mueller for there discovery in 1987, just one year after their big discovery. The point of this is that DFT is clearly NOT the end all, but nonetheless even in system were DFT/LDA does fail in some respects, it almost always gets many

other aspects of the properties correct! Therefore, DFT is almost always the best starting point when trying to understand any material.

The final comment is with regards to codes available to perform DFT calculations. The development of programming languages in the 1970s allowed one to develop codes which were portable and not dependent on the computer architecture. In the early years you could only perform these calculations if you had some serious infrastructure and know-how. It was really only for the initiated, not so different from a specialized experimental apparatus. Of course, now there are many available codes. You can download free, open source DFT codes such as ABINIT or PWSCF. Alternatively, you can purchase a DFT code called VASP, which is one of the most popular. All three of these codes are planewave pseudopotential codes. If you want to do LAPW calculations, you could purchase Wien. If you wanted to perform LMTO calculations you could download the free, open source code LMTART, etc, etc, etc.

3   Summary of perspective

Monumental advances have taken place in science, including the development of classical and quantum mechanics. In quantum mechanics, the many-body problem is quite intractable, and therefore we must use approximations. Luckily, reliable theories and approximations have been developed in DFT and LDA, respectively. Furthermore, reliable methods have been developed to treat the one-electron problem, such as pseudopotentials, LAPW, and LMTO. Fast computers are cheap and widely available, as are codes implementing DFT. Therefore, a reasonable investment in time and effort can bring all of these years of hard work and innovation to your disposal.