

An Introduction to Density Functional Theory

Andrew Valentini

Department of Physics, University of Florida, Gainesville, Florida, United States

(Dated: December 3rd, 2025)

Solutions to the Schrodinger equation determines a quantum mechanical system's physical properties, such as its time evolution and energy levels. Since materials are made up of multiple atoms, they are inherently a many-body quantum mechanical system. Solving the Schrodinger equation for materials to determine their physical properties quickly becomes an intractable task for realistic scenarios given the number of interactions that are necessary to consider. To solve the Schrodinger equation for many-body systems, a set of approximations are used to make the problem feasibly-solvable. The scheme that these approximations are carried out in is called density functional theory (DFT). This review article will detail the assumptions central to DFT and how calculations are carried out in current solid-state physics, computational chemistry, and materials science research.

I. INTRODUCTION

Central to quantum mechanics, the Schrodinger equation,

$$-i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t} = \hat{H}\Psi(\mathbf{r},t) \quad (1)$$

governs the time evolution of a quantum system's state $\Psi(\mathbf{r},t)$. Determining the wavefunction $\Psi(\mathbf{r},t)$ by solving the Schrodinger equation provides a complete description of a system, from which one can determine observables of the system and how these evolve in time. For many scenarios, the time evolution is often not of crucial interest, and one is instead interested in a state's time-independent properties, called stationary states. In these cases, the wavefunction is assumed to be a separable function of position and time, which reduces Eq. (1) to an eigenvalue problem for the stationary energy states of the system;

$$\hat{H}\Psi(\mathbf{r}) = E\Psi(\mathbf{r}) \quad (2)$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \quad (3)$$

is the Hamiltonian operator, which contains the kinetic and potential energy of the system of interest. Of particular interest is the ground-state energy E_0 , which is the lowest energy eigenvalue satisfying Eq. (2), since this is the energy at which a system will be most stable.

This procedure is carried out for a variety of simple single-particle and atomic scenarios throughout standard undergraduate and graduate courses on quantum mechanics for which analytic solutions for the state and its evolution can be analytically determined. More physically-realistic systems contain many particles and terms in the potential to account for, which makes exact analytic solutions impossible to find without applying simplifying assumptions.

Solving the Schrodinger equation for multi-atom systems is an especially difficult task, as these naturally give

rise to emergent phenomena such as correlations and statistical behavior.

The Hamiltonian for multi-atom systems consisting of electrons and nuclei can be written as

$$\hat{H} = \hat{T}_{\text{electrons}} + \hat{T}_{\text{nuclei}} + \hat{V}_{ee} + \hat{V}_{nn} + \hat{V}_{en}. \quad (4)$$

Since the interactions between electron-electron, nuclei-nuclei, and electron-nuclei pairs are all governed by the Coulomb potential, we can write the multi-atom Hamiltonian more explicitly as

$$\begin{aligned} \hat{H} = & -\sum_{i=1}^{N_e} \frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 - \sum_{I=1}^{N_n} \frac{\hbar^2}{2M_I} \nabla_{\mathbf{R}_I}^2 + \frac{1}{2} \sum_{i,j=1}^{N_e} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & + \frac{1}{2} \sum_{I,J=1}^{N_n} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I=1}^{N_e, N_n} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} \end{aligned} \quad (5)$$

where $|\mathbf{r}_i - \mathbf{r}_j|$ are the electron-electron distances, $|\mathbf{R}_I - \mathbf{R}_J|$ are the nuclei-nuclei distances, $|\mathbf{r}_i - \mathbf{R}_I|$ are the electron-nuclei distances, N_e is the number of electrons, N_n is the number of nuclei, m_e is the electron mass, M_I are the nuclei masses, e is the fundamental charge, and Z_I is the atomic number of the I -th nucleus.

From the Hamiltonian in Eq. (5), it is apparent that solving a multi-atom system is very computationally-intensive, so approximation techniques must be applied to the system's Hamiltonian and the wavefunction Ψ describing the full state of the multi-atom system. This paper will explain how the time-independent Schrodinger equation for many-atom systems is solved by first detailing all of the necessary approximations that need to be applied to simplify our problem. We will first briefly discuss two simplifications to our system of interest, called the Born-Oppenheimer approximation and the Hartree product, which make solving the time-independent Schrodinger equation for many-atom systems slightly less complicated. We will then detail the most powerful approximation technique, called density functional theory, which allows us to solve the time-independent Schrodinger equation through an iterative process, which will be clearly laid out at the end of this paper. We finally close this paper with how it is used in

modern research and its widespread impact in a variety of fields.

II. APPROXIMATION TECHNIQUES

A. Born-Oppenheimer Approximation

To begin simplifying the expression for our system, we first use the fact that the mass of electrons is much smaller than the mass of nuclei, meaning that the electrons will move much more quickly than the nuclei. This simplification, called the *Born-Oppenheimer approximation*, allows us to treat the nuclei as classical point charges relative to the electron dynamics, meaning one solves the Schrodinger equation for the electronic wavefunction and energy for a system with fixed nuclei. When we only consider the electronic wavefunction, our Hamiltonian is significantly reduced by ignoring the effect of the nuclei's kinetic energy \hat{T}_{nuclei} and the nuclei-nuclei potential V_{nn} in Eq. (5), leaving us with

$$\hat{H} = \hat{T}_{\text{electrons}} + \hat{V}_{ee} + \hat{V}_{en}. \quad (6)$$

B. Hartree Product

In only considering the electrons of a multi-atom system, the electronic wavefunction is a function of all $3N$ coordinates for an N -electron system;

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (7)$$

which captures correlations between all possible electron pairs. We can simplify our $3N$ -dimensional electronic wavefunction by instead considering N 3-dimensional electronic wavefunctions. This simplification is called the *Hartree product* [1], and this assumes a mean-field approximation where each electron moves in a field created by all other electrons. The Hartree approximation allows us to express the electronic wavefunction as

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_N(\mathbf{r}_N). \quad (8)$$

Even when using the Born-Oppenheimer approximation to reduce the complexity of the multi-atom Hamiltonian and the Hartree product to simplify the electronic wavefunction, solving the Schrodinger equation for multi-atom systems is still a very computationally-intensive task. For example, consider a single H_2O molecule. H_2O has $2 + 8 = 10$ electrons, meaning the Schrodinger equation for this single molecule would be a 30-dimensional problem. If we wished to solve for the dynamics and ground-state energy of a three-dimensional piece of ice made of only ten H_2O molecules in each spatial dimension, our system would have $10 \times 1,000 = 10,000$ electrons, meaning the Schrodinger equation for this simple solid would be a 30,000-dimensional problem. If we

wish to solve the Schrodinger equation for solids materials more realistic than our simple ice lattice, it is clear that a more powerful technique will be necessary.

The key step in allowing us to investigate the electronic structure of multi-atom systems is treating the three-dimensional *electron density* $n(\mathbf{r})$ as the fundamental variable that describes the state of a given system, rather than the $3N$ -dimensional wavefunction given in Eq. (8). Considering the electron density rather than the wavefunction leads to a formalism called **Density Functional Theory**. To reliably replace the wavefunction with the electron density and make solving for the ground state energy and other properties of multi-atom systems more realistic, we must demonstrate that the ground state of our system is uniquely determined by the electron density and find the equation governing its evolution.

C. Density Functional Theory

The electron density is the measure of probability of finding an electron at a specific point in space \mathbf{r} . We determine the electron density by integrating a many-electron probability density over the coordinates of all electrons except one:

$$n(\mathbf{r}) = N_e \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_{N_e}, \quad (9)$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_e})$ is a Hartree product wavefunction given in Eq. (8) and the prefactor N_e accounts for the contribution from each electron to ensure the density is properly normalized.

Though the electron density significantly reduces the dimensionality of our problem, its exact role in solving for the ground state energy and dynamics of multi-atom systems was not realized until Hohenberg and Kohn demonstrated two crucial theorems that would lay the groundwork of density functional theory [2].

The first Hohenberg and Kohn theorem states that the ground-state electron density $n_0(\mathbf{r})$ completely determines the external potential experienced by the electrons, $\hat{V}_{\text{ext}}(\mathbf{r})$. This external potential is generated by the electrostatic interaction between the nuclei and electrons, $\hat{V}_{\text{ext}}(\mathbf{r}) \equiv \hat{V}_{en}$, and determines the Hamiltonian of the system, as is shown in Eq. (6), meaning the ground-state electron density in principle provides enough information to construct all observables from it.

The second Hohenberg and Kohn theorem states that an energy functional that takes an electron density as an input $E[n(\mathbf{r})]$ will output a value that is always greater than or equal to the ground state energy. This implies that one can minimize this energy functional with respect to the electron density to find the ground state of the system. To find the form of $E[n(\mathbf{r})]$, we take the expectation value of the Hamiltonian of Eq. (6) and separate the term to do with the dynamics of electrons from

the external potential term:

$$\begin{aligned} E[n(\mathbf{r})] &= \langle \Psi | \hat{T}_{\text{electrons}} + \hat{V}_{ee} | \Psi \rangle + \langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle \\ &\equiv F[n(\mathbf{r})] + \int n(\mathbf{r}) \hat{V}_{\text{ext}}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (10)$$

where we used the definition of the electron density in Eq. (9) to write the expectation value of the external potential as an integral over the density. $F[n(\mathbf{r})]$, called the *exchange-correlation functional*, accounts for all the internal electronic energy contributions, and is in principle the same for all systems of electrons, so is called the universal function. The internal electronic energy contributions come from the electrons' kinetic and interaction energy, and as such, the universal function can be written as

$$F[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{\text{XC}}[n(\mathbf{r})]. \quad (11)$$

Because the interaction term $E_{\text{XC}}[n(\mathbf{r})]$ contains contributions from the quantum mechanical exchanges and correlations in our many-body system of electrons, the exact form of $F[n(\mathbf{r})]$ is unknown¹.

The ground-state energy minimizes the total energy functional, so when a variational method is applied to Eq. (10), the Kohn-Sham equations are derived

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \hat{V}_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i, \quad (12)$$

where

$$\hat{V}_{\text{eff}}(\mathbf{r}) = \hat{V}_{\text{ext}}(\mathbf{r}) + \hat{V}_{\text{Hartree}}[n(\mathbf{r})] + \hat{V}_{\text{XC}}[n(\mathbf{r})]. \quad (13)$$

The Kohn-Sham equations solve single-electron state ψ_i eigenvalue problems, and from these one builds the electron density using Eq. (9).

The three terms in the effective potential of Eq. (13) account for three separate contributions to the potential that an electron's wavefunction experiences under the set of approximations discussed earlier in this section. $V_{\text{ext}}(\mathbf{r})$ is the potential generated by the nuclei in the system, which we called \hat{V}_{en} earlier. $V_{\text{Hartree}}[n(\mathbf{r})]$ describes the classical electrostatic interaction between electrons in a many-body system, which arises from the Hartree product approximation given by Eq. (8). The final term, $V_{\text{XC}}[n(\mathbf{r})]$ contains the non-classical contributions from the exchange and correlations among electrons. It is derived by taking a functional derivative with respect to the electron density of the exchange-correlation energy term in Eq. (11). Because $E_{\text{XC}}[n(\mathbf{r})]$ must be approximated, the exact form of $V_{\text{XC}}[n(\mathbf{r})]$ is unknown.

With all of the necessary theory in place, the full scheme of density functional theory is as follows:

1. Guess a trial electron density $n(\mathbf{r})$

2. Build \hat{V}_{eff} using Eq. (13)

3. Solve for ψ_i using Eq. (12)

4. Build a new $n(\mathbf{r})$ from the derived ψ_i terms

5. Repeat until $n(\mathbf{r})$ converges to a ground state density $n_0(\mathbf{r})$

6. Use $n_0(\mathbf{r})$ to derive the ground-state energy E_0 using Eq. (10)

III. DFT IN PRACTICE

Toady, density functional theory is the standard method for simulating multi-atomic systems; a use which primarily spans a variety of solid state physics, computational chemistry, and materials science research. As explained in the body of this work, DFT relies on physical assumptions that reduces the complexity of the problem. Most researchers today use established, community-developed packages that carry out the computationally-intensive scheme detailed in the previous section rather than writing their own software. The most widely-used package is called the Vienna Ab initio Simulation Package (VASP) [5–7] due to its ability to produce very accurate results for a wide variety of materials without requiring the tuning of many parameters. Research groups buy licensing to VASP software and compile its code on high-performance computing clusters, since the amount of calculation that needs to be performed is nearly always too intense to be run on standard laptop processors. DFT simulations, most being carried out through VASP, have been used in a variety of scenarios, such as the prediction of accurate graphene's band structure [8], which describes how electrons move in a system and their associated energies, and the prediction of high temperature superconductors [9, 10]. An example of the fat band structure for graphene sitting on copper generated by VASP is given in Fig. 1.

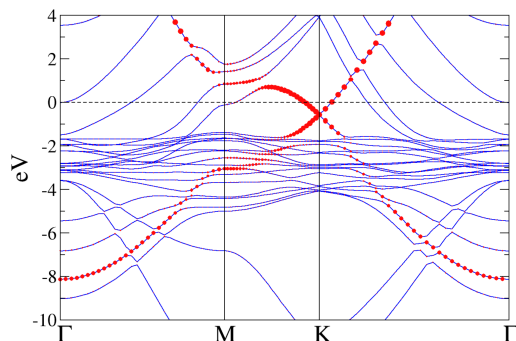


FIG. 1. Band structure generated by VASP DFT calculations for graphene on top of copper [11]

¹ See [3] and [4] for standard universal function approximations.

IV. CONCLUSION

Density functional theory, whose basic scheme has been outlined in this paper, provides a powerful framework for studying the electronic properties of multi-atom systems by replacing the many-body wavefunction with a three-dimensional electron density. This reformulation makes solving for physical properties of interest for multi-atom systems, such as ground state energies,

computationally-feasible. Though DFT simulations are computationally-intensive, the theory's approximations make the otherwise-intractable problem of solving the many-body Schrodinger equation possible with a great deal of accuracy and applicable for a wide range of materials. For these reasons, DFT has become ubiquitous in research on the structure and behavior of multi-atom systems, which spans solid state physics, computational chemistry, and materials science.

-
- [1] D. R. Hartree, The wave mechanics of an atom with a non-coulomb central field. part i. theory and methods, *Mathematical Proceedings of the Cambridge Philosophical Society* **24**, 89–110 (1928).
 - [2] P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* **136**, B864 (1964).
 - [3] V. Sahni, K. P. Bohnen, and M. K. Harbola, Analysis of the local-density approximation of density-functional theory, *Phys. Rev. A* **37**, 1895 (1988).
 - [4] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [5] G. Kresse and J. Hafner, Ab initio molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558 (1993).
 - [6] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
 - [7] G. Kresse and J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science* **6**, 15 (1996).
 - [8] A. K. Geim and K. S. Novoselov, The rise of graphene (2007), arXiv:cond-mat/0702595 [cond-mat.mtrl-sci].
 - [9] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer, Superconductivity of metallic boron in mgb_2 , *Physical Review Letters* **86**, 4656–4659(2001).
 - [10] N. Bernstein, C. S. Hellberg, M. D. Johannes, I. I. Mazin, and M. J. Mehl, What superconducts in sulfur hydrides under pressure and why, *Phys. Rev. B* **91**, 060511 (2015).
 - [11] C. A. Marianetti, Graphene on cu: Vasp procedure tutorial (fat bands), http://grandcentral.apam.columbia.edu:5555/tutorials/dft_procedures/fat_bands/graphene_on_cu/vasp/index.html, Columbia University, APAM Department.