Webinar 02 – Density Functional Theory (Part 1)

Polished summary of the feedback session

Overview

This session is the first of two feedback webinars on Density Functional Theory (DFT). In the past week, we focused on foundational concepts needed to construct DFT; the formalism itself will be developed in the next session. If DFT still feels abstract, that is expected at this stage.

1. Functions and Functionals

A functional takes a function as its argument and returns a number. By contrast, the derivative of a function (e.g., acceleration as the derivative of velocity) is still a function, not a functional. Classic examples of functionals include:

• The area under a curve: given a function f and bounds a and b, the integral ∫■■ f(x) dx maps the function f to a number. This is directly relevant in chemistry, where the area under a detector signal can be proportional to an analyte's amount.

• Point evaluation: the map f ■ f(a) assigns to each function its value at a fixed point a.

• Norms of functions: for instance, ||f|| defined via an integral produces a number for each function f.

• In physics: the action functional in Lagrangian mechanics; expectation values like total energy in quantum mechanics; and transforms (e.g., a single Fourier component at fixed frequency) when treated with one argument fixed.

2. The Schrödinger Equation

We revisited the equation's core components—the Hamiltonian, the wave function, and the total energy—and clarified common pitfalls.

2.1 Hamiltonian: Energy Contributions

The ab initio Hamiltonian for electrons and nuclei contains five and only five contributions: (i) kinetic energy of electrons; (ii) kinetic energy of nuclei; (iii) electron–nucleus attraction; (iv) electron–electron repulsion; and (v) nucleus–nucleus repulsion. Terms such as explicit spin–spin interactions or electron–phonon coupling do not appear as separate terms in the fundamental Hamiltonian. They can emerge in approximate treatments (e.g., Hartree–Fock) as effective interactions.

2.2 Wave Function: Domain and Target

For two spinless particles, the wave function maps six real position coordinates (■■) to complex numbers (■). Spin coordinates are absent because the particles are spinless. The modulus squared yields a real-valued probability density.

2.3 Total Energy as an Observable

The total energy E is measurable: it corresponds to the energy required to take a system from its ground state to a state where all particles are at rest at infinite separation.

3. The Born–Oppenheimer Approximation

The approximation assumes that electrons adjust instantaneously to (effectively) static nuclear positions. It remains valid for slow nuclear motion, such as elastic deformation or typical vibrational dynamics in solids, and often even when electron–phonon coupling influences material properties through quasi-static snapshots.

When and why it can fail:

• Fast nuclei: e.g., ion implantation (high-speed ions in crystals) or ultrashort laser/magnetic pulses (femto-/attosecond), where electrons cannot equilibrate during the interaction.

• Very light nuclei: systems involving hydrogen may require beyond–Born–Oppenheimer treatments because nuclear quantum effects become appreciable.

• Near-degenerate configurations: when two nuclear configurations have almost the same total energy and are separated by a low barrier, tunneling and rapid switching between configurations undermine the assumption of well-defined nuclear positions.

4. Hartree–Fock and Post–Hartree–Fock Methods

We briefly reviewed Hartree–Fock and its post–Hartree–Fock extensions. The Hartree–Fock ground state uses a single Slater determinant, which is not exact in general. Configuration Interaction (CI) expands the wave function as a sum of excited-state Slater determinants. A full CI expansion is, in principle, sufficient to represent any antisymmetric wave function, including the exact ground state, though it is typically computationally prohibitive.

5. External Potential

The external potential identifies the specific quantum system within the universal ab initio Hamiltonian. For the O■ molecule, it can be written as the sum of Coulomb interactions between an electron at position r and the two nuclei at positions r■ (each with charge +8e). Once the external potential is specified, the system is fully defined for the purpose of solving the electronic problem.

6. Electron Density

Integrating the electron density over all space yields the total number of electrons. For O■, this integral equals 16. Confusion sometimes arises from conflating charge density with wave-function normalization (which integrates to 1), but densities integrate to total charge (or total electron count).

7. Course Logistics and Next Steps

Participants are invited to submit a one-paragraph summary of the week and propose an exam question. Approximately 25 participants have signed up for the project; teams (around 6–9 groups) will be finalized and communicated by email. The software for the hands-on component should now be installed; any issues can be posted on Zulip. Next week, we will construct the DFT formalism and introduce convergence testing as a crucial practical step at the start of any new series of calculations.

Closing

Thank you for participating. Questions can be posted in the chat or on Zulip. See you next week for Part 2 on DFT.