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# Chapter 2 – Survey of theoretical methods

The following chapter will be an introduction of the theoretical methods used in a Chapters 5 and 6 of this dissertation, specifically the context of NWChem and its use time-dependent density functional theory (TD-DFT) and the reliability of the resulting calculations for the system discussed.

## Density Functional Theory (DFT) (3-4 pgs)

DFT historical context. Self-consistent field.

### Time-dependent density functional theory (TD-DFT)

The problem with modeling excited states is the many-body problem, so a large factor in choosing a level of theory depends on whether it can do a good (enough) job approximating excited state. However, this concern is only an issue if you are indeed dependent on excited states, such as simulated a pump-probe system of XES spectra.

Somewhere talk about hybrid functionals and Gaussian basis sets?

## Theoretical method for VtC-XES and XANES calculations (3 pgs)

DFT is the most popular way to calculate both XES and XAS spectra. The following section is an overview of available codes and their levels of theory, however it is neither a comprehensive list nor a complete discussion of the applications of each code. For a more complete discussion, see Nascimento, et al. [Nascimento, 2022] and Rana, et al. [Rana, 2022].

Starting with the “simplest” theory and going to the most sophisticated, we will start with atomic model codes, which include quanty and crispy. These codes use atomic cross-sections, multiplet theory with (mostly) fitted parameters, and model Hamiltonians. However, recent work has been done to remove these empirical parameters and replace them with *ab initio* calculated ones. (cite Charles’ paper, if published)

Next are the DFT level theories, which include WIEN2k, ABINIT, VASP, and CASTEP. These codes are accurate for ground state properties but are less reliable for excited states; they use a “final state rule” with a core hole. A more sophisticated code is FEFF, which uses quasi-particle Green’s function theory. FEFF is appropriate for excited states and is very efficient, but it is missing some many-body physics. These properties, along with its historical context and supported GUI, make it one of the most popular choices when calculation crystallographic structures.

Then there are the Bethe-Salpeter Equation (BSE) codes, which include Exc!ting and OCEAN. These are the most accurate but the most demanding. They are less established and less user friendly, although they are still missing some physics. Finally, there the most sophisticated quantum chemistry codes like MRCI, MRCC, CASPT2, and QMC. Although these codes are highly accurate, their complexity is basically intractable. For an overview of all codes and their theory levels, see Table 1.

|  |  |  |
| --- | --- | --- |
| **Code Name** | **Theory Level** |  |
| NWChem | Time-dependent DFT (TD-DFT) |  |
| Orca | Time-dependent DFT (TD-DFT) |  |
| VASP | DFT |  |
| FEFF | Real-space multiple-scattering theory |  |
| Ocean | Bethe-Salpeter Equation |  |
| FDMES | Finite Element |  |
| CTM4XAS | Mulitplet |  |
| Quanty | Multiplet |  |

Table 1 Overview of theoretical codes used for XAFS and XES calculations.

Cite successes and limitations

## NWChem: A closer look (3 pgs)

Explain under the hood/ more in more depth explanation of the theory in NWChem

## NWChem: The reliability of the results (3-5 pgs)

Cite examples

## NWChem: Implementation (maybe)

## References