Materials Modeling using DFT: Chapter 2

1 Motivation

- Properties of materials depend on their host structure. For example, this could be a different lattice type.
- When investigating electron–phonon interactions, we want to understand the linear response of our material, or perturb the self-consistent-field (SCF) potential due to the perturbation of atomic nuclei.
- Many electron and nuclei interactions $\Rightarrow$ Electronic Structure Theory (EST).
- Stationary electronic states are states of constant energy. We study such stationary states via the time-independent Schrödinger equation.
- A wavefunction is a probability amplitude. A probability density is the norm squared. This also represents a distribution. The probability is $|\Psi(\mathbf{r})|^2\, d\mathbf{r}$, where $d\mathbf{r}$ is the region in space that we are integrating over.

2 The Many-Body Wavefunction and Orbitals

What is an orbital? An orbital is defined by the spatial distribution and energy level of a wavefunction. Two electrons can occupy the same orbital only with a defined (opposite) spin – that is, a distinct set of quantum numbers.

- An eigenstate is an orbital.
- The presence of additional electrons modifies both the potential landscape and the energy, and this modifies the orbital shape.

The many-body wavefunction is written

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_N). \tag{1}$$

- Physically, it represents the probability amplitude of finding electron 1 at $\mathbf{r}_1$, and so on. It does not have a notion of distinguishability – this is *simultaneity*.
- **Total charge density:** this gives the probability of finding *any* electron at $\mathbf{r}$, regardless of label.

3 Total Electronic Charge Density

$$\rho(\mathbf{r}=\mathbf{r}_i) = \int |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_N)|^2\, d\mathbf{r}_2\, d\mathbf{r}_3 \cdots d\mathbf{r}_N\, d\mathbf{R}_1 \cdots d\mathbf{R}_N. \tag{2}$$

Thus,

$$\begin{aligned} n(\mathbf{r}) &= \int d\mathbf{r}_2 \cdots d\mathbf{r}_N\, d\mathbf{R}_1 \cdots d\mathbf{R}_N\, |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_N)|^2 \\ &\quad + \cdots + \int d\mathbf{r}_1 \cdots d\mathbf{r}_{N-1}\, d\mathbf{R}_1 \cdots d\mathbf{R}_N\, |\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_{N-1},\mathbf{r};\mathbf{R}_1,\ldots,\mathbf{R}_N)|^2 \\ &= N \int d\mathbf{r}_2 \cdots d\mathbf{r}_N\, d\mathbf{R}_1 \cdots d\mathbf{R}_N\, |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_N)|^2. \end{aligned} \tag{3}$$

This simplification is valid because electrons are indistinguishable. This means that all electrons are equally likely to be found in any of the N terms. Oftentimes, we normalize our states. Therefore,

$$\begin{aligned} \int n(\mathbf{r})\, d\mathbf{r} &= N \int d\mathbf{r}\, d\mathbf{r}_2 \cdots d\mathbf{r}_N\, d\mathbf{R}_1 \cdots d\mathbf{R}_N\, |\Psi(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N;\mathbf{R}_1,\ldots,\mathbf{R}_N)|^2 \\ &= 1 \cdot N = N. \end{aligned} \tag{4}$$

Thus, integrating our electronic charge density over all space returns the number of electrons in our system, since the integral of the norm squared of our wavefunction is one (unity).

4 The Many-Body Hamiltonian

With this many-body wavefunction, $\hat{H}\Psi = E_{\text{tot}}\Psi$. This means that our energy eigenvalue is now the total energy. The momentum operator for a single particle is $\hat{\mathbf{p}} = -i\hbar\nabla_{\mathbf{r}}$. The kinetic energy operator is

$$\hat{T} = \sum_i \frac{\hat{\mathbf{p}}_i^2}{2m_e} + \sum_I \frac{\hat{\mathbf{P}}_I^2}{2M_I} = \sum_i -\frac{\hbar^2}{2m_e}\nabla_i^2 + \sum_I -\frac{\hbar^2}{2M_I}\nabla_I^2. \tag{5}$$

Our potential is therefore

$$\begin{aligned} \hat{V}_{\text{tot}} &= V_{e\text{-}e} + V_{N\text{-}N} + V_{e\text{-}N} \\ &= \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{R}_I|}. \end{aligned} \tag{6}$$

The many-body Schrödinger equation is therefore

$$\begin{aligned} &\left[\sum_i \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_I \frac{-\hbar^2}{2M_I}\nabla_I^2 + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{r}_j|} \right. \\ &\left. + \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{R}_I|} \right] \Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{R}_1,\ldots,\mathbf{R}_N) = E\Psi. \end{aligned} \tag{7}$$

In reality, the number of nuclei is different from N (the number of electrons). We can also model time dependence, spin–orbit coupling (SOC), and other relativistic effects, and perhaps external $\mathbf{B}$-field or $\mathbf{E}$-field terms.

- The lowest energy eigenstate is the ground state. With the ground state we can predict many properties, such as enthalpies of formation, elastic properties, and thermal properties, among many others.
- The number of gridpoints needed to represent a problem grows exponentially with the number of atoms, or system size.

5 Atomic Units and the First-Principles Philosophy

- A first-principles approach means no external fitting parameters.
- 1 Ry is $\frac{1}{2}$ Ha. The energy of one Hartree is the Coulomb attraction of one electron–proton pair,

$$E_{\text{Ha}} = \frac{e^2}{4\pi\varepsilon_0 a_0}, \tag{8}$$

  where a_0 is the Bohr radius, i.e. the radius of a hydrogen atom.
- We can obtain a dimensionless expression for our many-body Schrödinger equation by dividing through by one Hartree. Thus, the Hartree is a natural unit with which to study microscopic phenomena.
- The only external parameters are the species masses and atomic numbers. This means the theory is fundamental. Where do these quantities come from?

Discussion Question

What is the difference between the Born–Oppenheimer approximation and the clamped-nuclei approximation?

In the clamped-nuclei approximation, we literally clamp the nuclei. That is, we do not consider their kinetic energy, and only consider the motion of the electrons; the nuclear positions instead enter as a parameter. The clamped-nuclei approximation enters as an ingredient of the Born–Oppenheimer approximation.

6 The Born–Oppenheimer / Clamped-Nuclei Approximation

The clamped-nuclei approximation is an ingredient of the Born–Oppenheimer approximation. The uncertainty principle prevents the nuclei from being perfectly immobile,

$$\Delta x \, \Delta p \geq \hbar. \tag{9}$$

We nonetheless assume that $M_I = \infty$. Thus,

$$E = E_{\text{tot}} - \sum_{I<J} \frac{Z_I Z_J e^2}{4\pi\varepsilon_0 |\mathbf{R}_I - \mathbf{R}_J|}, \tag{10}$$

and therefore

$$\left[-\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{R}_1, \ldots, \mathbf{R}_M) = E\Psi, \tag{11}$$

where the Hamiltonian is, of course, now written in natural (Hartree) units.

7 The Fundamental Equation of Electronic Structure Theory

We let

$$V_n(\mathbf{r}) = -\sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}, \tag{12}$$

so that

$$\left[-\sum_i \frac{\nabla_i^2}{2} + \sum_i V_n(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi = E\Psi. \tag{13}$$

The equation above is the fundamental equation of electronic structure theory. Written compactly,

$$\hat{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = -\sum_i \frac{\nabla_i^2}{2} + \sum_i V_n(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{14}$$

Let $\hat{H}_0(\mathbf{r}) = -\dfrac{\nabla^2}{2} + V_n(\mathbf{r})$. Then

$$\hat{H}(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_i \hat{H}_0(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{15}$$

$\hat{H}_0$ is the single-electron Hamiltonian.

7.1 Independent-Electron Approximation and the Hartree Approximation

Let $\dfrac{1}{2} \sum_{i \neq j} \dfrac{1}{|\mathbf{r}_i - \mathbf{r}_j|} = 0$. Then

$$\sum_i \hat{H}_0(\mathbf{r}_i)\, \Psi = E\Psi. \tag{16}$$

This Hamiltonian acts on each electron coordinate of Ψ one at a time. We approximate our many-body wavefunction as a simple product,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \phi_1(\mathbf{r}_1)\, \phi_2(\mathbf{r}_2) \cdots \phi_N(\mathbf{r}_N) = \prod_i \phi_i(\mathbf{r}_i). \tag{17}$$

This is known as the **Hartree approximation**. Therefore,

$$\sum_i \hat{H}_0(\mathbf{r}_i) \prod_j \phi_j(\mathbf{r}_j) = \prod_j \sum_i \hat{H}_0(\mathbf{r}_i)\, \phi_j(\mathbf{r}_j). \tag{18}$$

Case of two particles.

$$\begin{aligned} \prod_{j=1}^{2} \Big(\hat{H}_0(\mathbf{r}_1)\phi_j(\mathbf{r}_j) + \hat{H}_0(\mathbf{r}_2)\phi_j(\mathbf{r}_j) \Big) &= \Big(\hat{H}_0(\mathbf{r}_1)\phi_1(\mathbf{r}_1) + \hat{H}_0(\mathbf{r}_2)\phi_1(\mathbf{r}_1) \Big) \\ &\quad \times \Big(\hat{H}_0(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \hat{H}_0(\mathbf{r}_2)\phi_2(\mathbf{r}_2) \Big) \\ &= \Big(\varepsilon_1\phi_1(\mathbf{r}_1) + \hat{H}_0(\mathbf{r}_2)\phi_1(\mathbf{r}_1) \Big) \\ &\quad \times \Big(\hat{H}_0(\mathbf{r}_1)\phi_2(\mathbf{r}_2) + \varepsilon_2\phi_2(\mathbf{r}_2) \Big). \end{aligned} \tag{19}$$

Generalizing to N particles, the total energy is a simple sum of the single-particle eigenvalues:

$$E = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_N. \tag{20}$$

The independent-electron picture $\neq$ Hartree approximation.

The main limitations of the Hartree approximation:

- Wavefunctions do not account for the antisymmetric nature of fermion states.
- The Coulomb interaction is not included.

7.2 The Pauli Exclusion Principle and Slater Determinants

Pauli exclusion principle: the wavefunction changes sign under particle exchange.

To account for the Pauli exclusion principle, we must antisymmetrize our wavefunction when discussing fermions. This is done via a Slater determinant,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}\Big[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\Big] = \frac{1}{\sqrt{2}}\begin{vmatrix}\phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1)\\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2)\end{vmatrix}. \tag{21}$$

The orbital index increases along the columns, and the position index increases along the rows. For $N > 2$ electrons, the prefactor of our Slater determinant is $\frac{1}{\sqrt{N!}}$; this prefactor ensures the proper normalization.

For two electrons, the density is

$$\begin{aligned} n(\mathbf{r}) &= \int d\mathbf{r}_2\, |\Psi(\mathbf{r}, \mathbf{r}_2)|^2 = \int d\mathbf{r}\, d\mathbf{r}_2\, \Psi^*(\mathbf{r}_1, \mathbf{r}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2) \\ &= \frac{1}{2}\int d\mathbf{r}_2 \Big[\phi_2^*(\mathbf{r}_2)\phi_1^*(\mathbf{r}) - \phi_2^*(\mathbf{r})\phi_1^*(\mathbf{r}_2)\Big]\Big[\phi_1(\mathbf{r})\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r})\Big] \\ &= \frac{1}{2}\int d\mathbf{r}_2\, |\phi_1(\mathbf{r})|^2|\phi_2(\mathbf{r}_2)|^2 + |\phi_1(\mathbf{r}_2)|^2|\phi_2(\mathbf{r})|^2 \\ &= \frac{1}{2}\left[|\phi_1(\mathbf{r})|^2 \int d\mathbf{r}_2 |\phi_2(\mathbf{r}_2)|^2 + |\phi_2(\mathbf{r})|^2 \int d\mathbf{r}_2 |\phi_1(\mathbf{r}_2)|^2\right] \\ n(\mathbf{r}) &= |\phi_1(\mathbf{r})|^2 + |\phi_2(\mathbf{r})|^2 \qquad \text{(assumes our single-particle states are renormalized).} \end{aligned} \tag{22}$$

- The index on the orbital corresponds to the electron label.
- $\phi_1(\mathbf{r}_2) \Rightarrow$ electron 1 at position $\mathbf{r}_2$.

8 The Mean-Field (Hartree) Approximation

Can we maintain a single-particle approximation while accounting for the Coulomb interaction? The answer is yes, via the mean-field approximation – that is, via the Hartree potential.

$$\nabla^2\phi(\mathbf{r}) = 4\pi n(\mathbf{r}) \quad \Rightarrow \quad \text{the electronic charge distribution } n(\mathbf{r}) \text{ generates an electrostatic potential at } \mathbf{r}. \tag{23}$$

Electrons submerged in this electrostatic potential have an electrostatic potential energy

$$V_H(\mathbf{r}) = -\phi(\mathbf{r}) \qquad \text{(in Hartree units)}, \tag{24}$$

$$\nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}), \qquad V_H(\mathbf{r}) = \int d\mathbf{r}' \, \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{25}$$

so that the Hartree potential is simply the Coulomb potential in Hartree units.

A volume element $d\mathbf{r}'$ with charge $dQ = -d\mathbf{r}' \, n(\mathbf{r}')$ generates a potential $dV(\mathbf{r}) = dQ/|\mathbf{r} - \mathbf{r}'|$ at $\mathbf{r}$:

$$dV = \frac{-n(\mathbf{r}') \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \tag{26}$$

Always pay special attention to the infinitesimal and the integrand – it always has physical meaning. We can then use this term in our single-particle Hamiltonian to improve the approximation:

$$\hat{H}_0(\mathbf{r}) = \frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}).^1 \tag{27}$$

The Schrödinger equation is $\hat{H}\phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i)$, i.e.

$$\left[\frac{\nabla_i^2}{2} + V_n(\mathbf{r}_i) + V_H(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i), \tag{28}$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2, \qquad \nabla^2 V_H = -4\pi n(\mathbf{r}). \tag{29}$$

The new equations we have are

$$\left[-\frac{\nabla_i^2}{2} + V_n(\mathbf{r}_i) + V_H(\mathbf{r}_i) \right] \phi_i(\mathbf{r}_i) = \varepsilon_i \phi_i(\mathbf{r}_i), \qquad n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2, \qquad \nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}). \tag{30}$$

The Hartree potential is the average potential felt by each electron.

We therefore call this approximation the **mean-field approximation**, because we encode the Coulomb interaction via a Hartree potential, which is an average potential felt by each electron. The system of equations is solved self-consistently:

1. Make an ansatz for our wavefunctions.
2. Construct our charge density.
3. Obtain the Hartree potential.
4. Diagonalize the Hamiltonian to obtain updated eigenstates and eigenvalues.

- DFT: a $3N$-dimensional problem $\rightarrow$ N three-dimensional simultaneous problems.
- **This approximation would be good if electrons were classical particles.**
- **This method is used in the study of astrophysical plasmas and transport.**
- We want to add the exchange and correlation potential.

[1] The notes write the kinetic term here as $+\nabla^2/2$; a few lines later, in Eq. (30), it is correctly written as $-\nabla^2/2$. Transcribed as written.

9 The Hartree–Fock Equations

- We want to maintain a Slater-determinant ansatz.
- To do this, we must assume that electron–electron interactions are weak.

We do this using the variational principle. Consider

$$\hat{H}\Psi = E\Psi, \qquad E = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \; \Psi^* \hat{H} \Psi \equiv \langle \Psi | \hat{H} | \Psi \rangle. \tag{31}$$

We want to minimize E with respect to variations in $\phi_i(\mathbf{r}_i)$,

$$\frac{\delta E}{\delta \phi_i^*(\mathbf{r})} = 0, \qquad \int d\mathbf{r} \; \phi_i^*(\mathbf{r}) \phi_j(\mathbf{r}) = \delta_{ij}. \tag{32}$$

We obtain the Hartree–Fock equations,

$$\left[-\frac{\nabla^2}{2} + V_n(\mathbf{r}) + V_H(\mathbf{r}) \right] \phi_i(\mathbf{r}) + \int d\mathbf{r}' \; V_x(\mathbf{r}, \mathbf{r}') \, \phi_i(\mathbf{r}') = \varepsilon_i \phi_i(\mathbf{r}), \tag{33}$$

$$n(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2, \qquad \nabla^2 V_H(\mathbf{r}) = -4\pi n(\mathbf{r}). \tag{34}$$

The Hartree–Fock approach introduces the exchange term when minimizing E with respect to variations in ϕ, subject to wavefunction orthonormality. Additionally, we assume wavefunctions described by a Slater determinant.

$$V_x(\mathbf{r}, \mathbf{r}') = -\sum_j \frac{\phi_j^*(\mathbf{r}') \, \phi_j(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \qquad \Rightarrow \qquad \text{nonlocal.} \tag{35}$$

The exchange potential arises from the Pauli exclusion principle, and prevents two electrons from occupying the same quantum state.