

Why quantum mechanics?

- The behavior of the particles is governed by the equation of motion, and its classical mechanical version is known as Newton's law.
- The proper description of atoms, molecules, and electrons is given by the laws of quantum mechanics. For this reason, we need to consider the **Schrödinger equation**, which is a quantum-mechanical equation of motion.
- If the solutions of the Schrödinger equations are generated without reference to experimental data, the methods are usually called "ab initio" (Latin: "from the beginning") or "first principle".

The Schrödinger equation

- In solid-state physics, the fundamental interaction we are interested in is the electrostatic interaction.
- Here we introduce three assumptions to the SE
 - i. time-independent
 - ii. non-relativistic
 - iii. Born-Oppenheimer approximation
- Under these approximations, the system of nuclei and electrons is described with a Hamiltonian below

$$\hat{H} = T_{\text{nuc}} + T_{\text{el}} + V_{\text{nuc-nuc}} + V_{\text{nuc-el}} + V_{\text{el-el}}$$

Hamiltonian

- The terms in Hamiltonian are written in the atomic unit as

$$T_{\text{nuc}} = \sum_{I=1}^L \frac{\nabla_I^2}{2M_I} \quad (\text{kinetic energy of nuclei})$$

$$T_{\text{el}} = \sum_{i=1}^N \frac{\nabla_i^2}{2} \quad (\text{kinetic energy of electrons})$$

$$V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (\text{nuclei-nuclei repulsion})$$

$$V_{\text{nuc-el}} = - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (\text{nuclei-electron attraction})$$

$$V_{\text{el-el}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (\text{electron-electron repulsion})$$

- Note that $V_{\text{el-el}}$ is the two-electron operator. Other operators are one-electron operator.

Dirac's bracket notation

- It is convenient to use Dirac's "bra-ket notation" for wave functions and multi-dimensional integrals in electronic structure theory to simplify the notation. The equivalences are defined as

$$\begin{aligned} |\Psi\rangle &\equiv \Psi, \quad \langle\Psi| \equiv \Psi^* \\ \int d\mathbf{r} \Psi^* \Psi &= \langle\Psi|\Psi\rangle \\ \int d\mathbf{r} \Psi^* \hat{H} \Psi &= \langle\Psi|\hat{H}|\Psi\rangle \end{aligned}$$

- The ket $|\Psi\rangle$ denotes a wave function while the bra $\langle\Psi|$ denotes a complex conjugate wave function Ψ^* . The combined bracket denotes that the whole expression should be integrated over all coordinates.

Effective Hamiltonian

- Except for the simplest cases, there are no simple ways to solve the SE in a closed analytical form so we have to solve it numerically.
- The SE is a second-order partial differential equation (PDE), so in principle, it can be directly solved. However, this needs integration over a large number of dimensions ($3 \times N_{\text{elec}}$), which is impossible.
- This difficulty can be solved by two approaches
 - i. Approximate the electron-electron interaction by the effective one-electron problem. This reduces the $3N$ dim. integration to a sum of 3 dim. integrations. Here the original Hamiltonian reduces to the effective Hamiltonian.
 - ii. Expanding the wave function in some suitable basis set, because this will convert the PDE into a set of algebraic equations.

- Depending on the form of the effective Hamiltonian, we have the **Hartree-Fock equation** or the **Kohn-Sham equation**.
- The former is used in the Hartree-Fock and post-Hartree-Fock theories, and the latter is used in the density functional theory (DFT).

Hartree product

- As a simple example of deriving the effective hamiltonian, we will review the case with using the Hartree product as a wavefunction.
- We are mainly interested in the electronic ground state energy E_0 .
- There is an important quantum mechanical principle - the *Rayleigh-Ritz variational principle* - that provides a route to find approximate solutions for E_0 .
- It states that the expectation value of \hat{H} of any Ψ is always higher than or equal to the exact E_0 , i.e.

$$E_0 \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

- So, the expectation value calculated by your "trial" wave function Ψ will always be an upper bound for the true ground state energy. By improving $|\Psi\rangle$, you will have a lower expectation value that is closer to the true ground state energy.

- Since $V_{\text{nuc-el}}$ is an **external potential** for an electron, we write it as $\hat{v}_{\text{ext}}(\mathbf{r})$ which is a function of \mathbf{r} .

$$\hat{v}_{\text{ext}}(\mathbf{r}) = - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

- Also, we define the one-electron Hamiltonian \hat{h} as

$$\hat{h}(\mathbf{r}) = -\frac{\nabla^2}{2} + \hat{v}_{\text{ext}}(\mathbf{r})$$

- Then one can form the one-electron SE as

$$\hat{h}(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

- In this case, the N -electron wave function can be expressed by the product of ψ_i as

$$\Psi_{\text{HP}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdots \psi_N(\mathbf{r}_N)$$

- This wave function is called the **Hartree product**, and it is the first crude guess for the true N -electron wave function.
- Note that ψ_i is orthonormal thus $\langle \psi_i(\mathbf{r}) | \psi_j(\mathbf{r}) \rangle = \delta_{ij}$.

Spatial and spin orbitals

- The one-electron wave function $\psi_i(\mathbf{r})$ is called the *orbital*, and the Hartree product means that N -electron wave function is expressed by the product of orbitals.
- Up to now, we assumed that the orbital depends only on \mathbf{r} , but an electron has the spin degree of freedom. We write this spin variable by ω , and combine it with the spatial coordinate \mathbf{r} as $\mathbf{x} = (\mathbf{r}, \omega)$.

- Let the one-electron wave function in \mathbf{x} as $\chi_i(\mathbf{x})$.
- Assuming that \mathbf{r} and ω are independent, we have $\chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\sigma_i(\omega)$, where ψ and σ denote the spatial and spin parts.
- χ, ϕ, σ are a spin-orbital, spatial orbital, and spin function.
- Since an electron has no chance to take both α and β spin simultaneously, following integration over the spin variable holds.

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = 1$$

$$\int d\omega \beta^*(\omega) \beta(\omega) = 1$$

$$\int d\omega \alpha^*(\omega) \beta(\omega) = 0$$

$$\int d\omega \beta^*(\omega) \alpha(\omega) = 0$$

Hartree equation

- Using the spin orbital χ above, we determine the expectation value of the Hamiltonian

$$\hat{H} = \hat{h}(\mathbf{r}) + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with respect to the Hartree product. This becomes

$$\begin{aligned} \langle \Psi_{\text{HP}} | \hat{H} | \Psi_{\text{HP}} \rangle &= \sum_{i=1}^N \int d\mathbf{x} \chi_i^*(\mathbf{x}) \hat{h}(\mathbf{r}) \chi_i(\mathbf{x}) \\ &+ \frac{1}{2} \sum_{i=1}^N \int d\mathbf{x} d\mathbf{x}' \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_i(\mathbf{x}) \chi_j(\mathbf{x}') \\ &+ V_{\text{nuc-nuc}} \end{aligned}$$

- Now we minimize this w.r.t. $\chi_i(\mathbf{x})$ under the constraint that $\chi_i^*(\mathbf{x})$ is normalized.
- This is a typical variational problem with the constraint taken into account via *Lagrange multipliers*, which gives

$$\frac{\delta}{\delta \chi_i^*} \left[\langle \Psi_{\text{HP}} | \hat{H} | \Psi_{\text{HP}} \rangle - \sum_{i=1}^N \{ \epsilon_i (1 - \langle \chi_i | \chi_i \rangle) \} \right] = 0$$

- The ϵ_i act as Lagrange multipliers ensuring the normalization of $\chi_i(\mathbf{x})$. This leads to the so-called **Hartree equation** as

$$\left[\hat{h} + \sum_{j=1}^N \int d\mathbf{x}' \chi_j^*(\mathbf{x}') \chi_j(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x})$$

- This shows that an effective one-electron SE is solved for an electron embedded in the electrostatic field of all electrons (including itself).

Hartree potential

- Using the electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

the *Hartree potential* \hat{v}_H can be defined as

$$\hat{v}_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- This corresponds to the mean-field effect of electron-electron repulsion from all electrons, but it does not capture the quantum effect such as exchange and correlation.
- With \hat{v}_H , the Hartree equation can be written as

$$\left[\hat{h} + \hat{v}_H \right] \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x})$$

Self-consistent field

- The Hartree equation has the form of one-electron SE. However, the solutions $\chi_i(\mathbf{x})$ enter the effective one-particle Hamiltonian via \hat{v}_H .
- This dilemma can be resolved by using an iterative algorithm: One starts with some initial guess for the wave functions that form the effective one-particle Hamiltonian. The Hartree equations are then solved and a new set of solutions are determined.
- This cycle is repeated so often until the iterations no longer modify the solutions, i.e. self-consistency is reached. Such a method is known as the **self-consistent field (SCF)** method.

Kohn-Sham equation

- Kohn and Sham considered what occurs if the electrons are non-interacting.
- In this case, the electron-electron repulsion is turned off, so the Schrodinger equation becomes the one-particle problem.
- The **Kohn-Sham equation** is defined by a local effective external potential in which the non-interacting particles move, typically denoted as $v_s(\mathbf{r})$ or $v_{\text{eff}}(\mathbf{r})$, called the Kohn-Sham potential.
- The solution to the Kohn-Sham equation is the single Slater determinant constructed from a set of orbitals that are the lowest-energy solutions to

$$\left[\hat{h} + \hat{v}_{\text{KS}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r})$$

- The Kohn–Sham potential \hat{v}_{KS} is

$$\hat{v}_{\text{KS}}(\mathbf{r}) = \hat{v}_{\text{ext}}(\mathbf{r}) + \hat{v}_H(\mathbf{r}) + \frac{\delta E_{\text{XC}}[\rho]}{\delta \rho(\mathbf{r})}$$

- $E_{\text{XC}}[\rho]$ in the last term is called the **exchange–correlation (XC) functional**. The quantum-mechanical effect comes via this term.
- The exact form of E_{XC} is not yet determined, so we need to model (or approximate) it. This is the reason why we have many XC functionals (such as PBE, BLYP, B3LYP, etc.)