Introduction to the Density Functional Theory

WS 2009

Roser Valentí
Institut für Theoretische Physik
Universität Frankfurt

Latex: Kateryna Foyevtsova
Chapter 1

Hamilton operator for a solid

The properties of matter are determined by the interaction of electrons and atomic nuclei (10^{23} particles/cm^3) and therefore the starting point for a quantitative theoretical description of a solid state system is the many-body Schrödinger equation. During formation of a crystal from individual atoms, only valence electrons participate in chemical bonding and the electrons near the nucleus, which occupy closed shells, are expected to have only a minor effect on the properties of the system.

We will consider the following notation:

\[ \vec{p} \quad \text{electron impulse} \]
\[ \vec{P} \quad \text{ion impulse} \]
\[ N \quad \text{number of electrons} \]
\[ M \quad \text{number of ions} \]

A neutral atom consists of
- a positive spherically symmetric ion carrying charge \( Z_v e \) and
- \( Z_e \) valence electrons.

1.1 Stationary Schrödinger equation

1) The kinetic energy of electrons is given by:

\[ T^e = \sum_{k=1}^{N} \frac{\vec{p}_k^2}{2m}. \]

2) The kinetic energy of ions is:

\[ T^I = \sum_{l=1}^{M} \frac{\vec{P}_l^2}{2M_I}. \]
3) The electron-electron interaction (in SI system):

\[ V_{e-e}(\{\vec{r}_k, \sigma_k\}) = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{\substack{k, k' \in \mathbb{N} \setminus \{k\}}} e^2 |\vec{r}_k - \vec{r}_{k'}|, \]

where \( \{\vec{r}_k, \sigma\} = \vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2, \vec{r}_3, \sigma_3, \ldots, \vec{r}_N, \sigma_N. \)

Here we only considered the Coulomb electrostatic interaction and we neglect relativistic effects.

4) The interaction between ions is:

\[ V_{\text{Ion-Ion}}(\{\vec{R}_I\}) = \frac{1}{2} \frac{1}{4\pi\varepsilon_0} \sum_{I, J \setminus I} \frac{e^2}{|\vec{R}_I - \vec{R}_J|} Z_{v_I} Z_{v_J}, \]

Here we assumed that the ions don’t come close to each other, i.e. there is no overlap among them. It is then possible to describe their potential as \( \frac{Ze^2}{R} \left( \frac{1}{4\pi\varepsilon_0} \right). \) In the case of overlap, the *frozen-core approximation* is not anymore valid.

5) The electron-ion interaction (without nuclear spin) can be written as:

\[ V_{e-Ion}(\{\vec{r}_k, \sigma_k\}; \{\vec{R}_I\}) = \sum_{I=1}^{M} \sum_{k=1}^{N} v_{\text{Ion}}(|\vec{R}_I - \vec{r}_k|), \]

We can now define the ion charge desity \( en^+(\vec{r}) \) as:

\[ \sum_{I=1}^{M} v_{\text{Ion}}(|\vec{R}_I - \vec{r}|) = -\frac{e^2}{4\pi\varepsilon_0} \int \frac{n^+(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' = v(\vec{r}). \]

where \( en^+(\vec{r}) \) contains the charge of nuclei as well as core electrons and the electron-ion interaction can be then written as:

\[ V_{e-Ion} = \sum_{k=1}^{N} v(\vec{r}_k). \]

The many-body stationary Schrödinger equation for the solid state system is then:

\( (T^e + T^{\text{Ion}} + V^{e-e} + V^{e-Ion} + V^{\text{Ion-Ion}})\Psi = E\Psi \quad (H\Psi = E\Psi). \)

The wavefunction \( \Psi = \Psi(\{\vec{r}_k, \sigma_k\}, \{\vec{R}_l\}) \) depends on all the electrons coordinates and all nuclei coordinates.
1.2 Separation of electron and lattice variables

The $V_{e-\text{ion}}$ term prevents the separation of $H$ into nuclear and electronic parts. Such a separation would allow us to write the solid state wavefunction as a product of nuclear and electronic wavefunctions.

We therefore introduce the Born-Oppenheimer approximation. This approximation rests on the fact that the nuclei are much more massive than the electrons, which enables us to say that the nuclei are nearly fixed with respect to electron motion. We can fix $\vec{R}$, the nuclear configuration at some value $\vec{R}_I$, and solve for the electronic wavefunction which depends only parametrically on $\vec{R}$. Repeating this procedure for a range of $\vec{R}$, we obtain the potential energy curve along which the nuclei move.

The Schrödinger equation for the electrons is then:

\[
H^e(\{\vec{R}_I\})\Phi_\nu(\{\vec{R}_I\}, \{\vec{r}_k, \sigma_k\}) = E^e_\nu \Phi_\nu;
\]

\[
H^e = T^e + V_{e-e} + V_{e-\text{ion}} \quad \text{for} \quad M_I/m \rightarrow \infty;
\]

\[
\Psi = \sum_\nu \Lambda_\nu(\{\vec{R}_I\})\Phi_\nu(\{\vec{R}_I\}, \{\vec{r}_k, \sigma_k\}). \tag{1.1}
\]

The arguments $\{\vec{R}_I\}$ in the electron wavefunction are to be interpreted as fixed parameters. For each set of atomic positions $\{\vec{R}_I\}$, the eigenvectors of $H^e$ form a complete basis of wavefunctions.

We want to analyze

\[
H\Psi = E\Psi \tag{1.3}
\]

If the operator $\Theta$ were one of the operators $T^e$, $V_{e-e}$ or $V_{e-\text{ion}}$, we would have

\[
\Theta(\Lambda_\nu\Phi_\nu) = \Lambda_\nu\Theta \Phi_\nu,
\]

which, however, does not hold for $T_{\text{ion}}$ since $T_{\text{ion}} = f(\vec{R}_I)$. $T_{\text{ion}} \propto \nabla^2_{\vec{R}_I}$.

Let us analyze $\nabla^2_{\vec{R}_I}(\Lambda_\nu\Phi_\nu(\vec{r}_k, \sigma_k))$:

\[
\nabla^2(ab) = a\nabla^2b + b(\nabla^2a) + 2(\nabla a)(\nabla b),
\]

\[
\nabla^2_{\vec{R}_I}(\Lambda_\nu\Phi_\nu) = \Lambda_\nu(\nabla^2_{\vec{R}_I}\Phi_\nu) + 2(\nabla_{\vec{R}_I}\Lambda_\nu)(\nabla_{\vec{R}_I}\Phi_\nu) + (\nabla^2_{\vec{R}_I}\Lambda_\nu)\Phi_\nu.
\]

We multiply Eq. [?] from the left by $\Phi^*_\mu$:
\[
(E_e^\mu + T^{\text{Ion}} + V^{\text{Ion-ion}})\Lambda_\mu \\
+ \sum_\nu \sum_{I=1}^M -\frac{\hbar^2}{2M_I} \left\{ \langle \Phi_\mu | \nabla^2_{\vec{R}_I} | \Phi_\nu \rangle \Lambda_\nu + 2 \langle \Phi_\mu | \nabla_{\vec{R}_I} | \Phi_\nu \rangle \nabla_{\vec{R}_I} \Lambda_\nu \right\} \\
= E_\mu \Lambda_\mu.
\]

The terms in the box above describe the electron-phonon coupling. There is an equation for each electronic state \( \Phi_\mu, E^e \) and these equations are coupled. This coupling of different electronic states is realized through lattice dynamics.

The electron-phonon coupling plays an important role for some properties in solid state systems. For instance,
- it is essential to explain the origin of conventional superconductivity (BCS (Bardeen-Cooper-Schrieffer))
- it is responsible for the Kohn anomaly, Jahn-Teller effect or the Peierls instability to cite a few phenomena.

**Approximations:**

1) We assume that the electrons at every time \( t \) and for each lattice geometry \( \{ \vec{R}_I \} \) are in an eigenstate of \( H^e \), i.e., the lattice motion should not cause any transition from \( \Phi_\mu \) to \( \Phi_\nu \):

\[
\langle \Phi_\mu | \nabla^2_{\vec{R}_I} | \Phi_\nu \rangle = 0,
\]

\[
\langle \Phi_\mu | \nabla_{\vec{R}_I} | \Phi_\nu \rangle = 0, \quad \mu \neq \nu.
\]

This is the Born-Oppenheimer approximation also called adiabatic approximation.

2) Diagonal terms:

a) Terms with \( \nabla_{\vec{R}_I} \):

\[
\langle \Phi_\mu | \nabla_{\vec{R}_I} | \Phi_\mu \rangle = \frac{1}{2} \nabla_{\vec{R}_I} \langle \Phi_\mu | \Phi_\mu \rangle = 0;
\]

\[
\Theta \langle \alpha | \alpha \rangle = \langle \Theta \alpha | \alpha \rangle + \langle \alpha | \Theta | \alpha \rangle = 2 \langle \alpha | \Theta | \alpha \rangle.
\]

b) Terms with \( \nabla^2_{\vec{R}_I} \):

\[
-\frac{\hbar^2}{2M_I} \langle \Phi_\mu | \nabla^2_{\vec{R}_I} | \Phi_\mu \rangle.
\]
\( \Phi \mu \) are only “indirectly” dependent on the atomic positions. The strongest dependence would be that each electron follows “its” atom without delay. Therefore,

\[
\Phi \mu \left( \{ \vec{R}_I \} , \{ \vec{r}_k , \sigma_k \} \right) \approx \Phi \mu \left( \{ \vec{r}_k - \vec{R}_I \} , \sigma_k \right) .
\]

Then,

\[
\langle \Phi \mu | \nabla^2 \vec{R}_I | \Phi \mu \rangle \approx \langle \Phi \mu | \nabla^2 \vec{r}_k | \Phi \mu \rangle ;
\]

\[
- \frac{\hbar^2}{2M_I} \langle \Phi \mu | \nabla^2 \vec{R}_I | \Phi \mu \rangle \approx \frac{m}{M_I} \langle \Phi \mu | - \frac{\hbar^2}{2m} \nabla^2 \vec{r}_k | \Phi \mu \rangle
\]

\[
\approx 10^{-4} \times \text{kinetic energy of the electron}
\]

this term can be neglected.

Therefore, with the variable separation:

\[
\Psi = \sum_\nu \Lambda_\nu \left( \{ \vec{R}_I \} \right) \Phi_\nu \left( \{ \vec{R}_I \} , \{ \vec{r}_k , \sigma_k \} \right) ,
\]

we are left in the Born-Oppenheimer approximation with two decoupled equations: one for the ion system

\[
(T^{\text{Ion}} + V^{\text{Ion-Ion}} + E^{e}_\mu) \Lambda_\mu = E\Lambda_\mu
\]

and one for the electron system

\[
H^e \Phi_\nu (\vec{r}_i , \sigma_i) = E^{e}_\nu \Phi_\nu (\vec{r}_i , \sigma_i) , \tag{1.4}
\]

with

\[
H^e = \sum_{k=1}^N - \frac{\hbar^2}{2m} \nabla^2 \vec{r}_k + \sum_{k=1}^N v(\vec{r}_k) + \frac{1}{2} \frac{1}{4\pi \varepsilon_0} \sum_{k \neq k'} \frac{e^2}{\mid \vec{r}_k - \vec{r}_{k'} \mid} ,
\]

Here, \( v(\vec{r}_k) \) is the potential due to the lattice, which plays a role of an “external potential”; \( \Phi_\nu (\{ \vec{r}_i , \sigma_i \} ) \) is a many-body wavefunction depending on \( 3N \) spatial coordinates and \( N \) spin coordinates.

We shall consider in the following the electron system.

If the electron interaction were given as

\[
V^{e-e} = \sum_k v^{e-e}(\vec{r}_k) ,
\]

we could solve the equation (1.4) since in this case we would have \( 10^{23} \) decoupled equations. BUT, \( V^{e-e} \) is a Coulomb interaction: it is long-ranged and, for short distances, very strong, and many of the interesting phenomena in solid state physics come precisely from this electron-electron interaction!!.