Ab initio electronic structure theory of extended systems: periodicity and electron repulsion

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Electronic structure theory

- Solving the electronic structure problem for molecules or solids consists in solving the electronic \textit{Schrödinger equation},

\[ \hat{H} \Psi_I = E_I \Psi_I. \]

- The electronic wavefunction \( \Psi_I \equiv \Psi_I (r_1, r_2, \ldots, r_N) \) depends on the position (and spin) of the \( N \) electrons.

- \( \hat{H} \) is the \textit{Hamiltonian} operator.

- There is in principle an infinite number of solutions.

- The solution with the \textit{lowest energy} (usually labelled as \( I = 0 \)) is referred to as the \textit{ground-state} solution.

- The higher-energy solutions (\( I > 0 \)) are the excited-state solutions.

- In this course, we will work within the \textit{Born–Oppenheimer approximation}.
Electronic structure theory

- In other words, the positions of the nuclei will be *fixed* while we are solving the Schrödinger equation for the electrons.

- Vibronic effects will not be discussed.

- The $N$-electron Hamiltonian reads $\hat{H} = \hat{T} + \hat{W}_{ee} + \hat{V}_{ne}$ where

$$
\hat{T} \equiv -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla^2 r_i = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right) \rightarrow \text{kinetic energy}
$$

$$
\hat{W}_{ee} \equiv \sum_{i<j}^{N} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|} \times \rightarrow \text{two-electron repulsion}
$$

$$
\hat{V}_{ne} \equiv \sum_{i=1}^{N} v_{ne}(r_i) \times \rightarrow \text{electron-nuclei attraction}
$$

where

$$
v_{ne}(r) = -\sum_{A}^{\text{nuclei}} \frac{Z_A e^2}{4\pi\varepsilon_0 |r - R_A|}
$$

- Note that the operators are written in *SI units.*
Atomic units

It is convenient to use unitless coordinates and energies where the Bohr radius

\[ a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2} \approx 0.529\text{Å} \]

and twice the ionization energy of the hydrogen atom

\[ E_I = \frac{m_e e^4}{2(4\pi\varepsilon_0)^2 \hbar^2} \approx 13.6\text{ eV} \]

are used as reference:

\[
\begin{align*}
x & \rightarrow \tilde{x} = x/a_0 \\
y & \rightarrow \tilde{y} = y/a_0 \\
z & \rightarrow \tilde{z} = z/a_0 \\
E & \rightarrow \tilde{E} = E/(2E_I)
\end{align*}
\]

This is the system of so-called atomic units (a.u.).
Atomic units

- In practice, the "tilde" symbol is dropped.

- It can be shown that, when atomic units are employed, the Hamiltonian looks like if \( \hbar = m_e = e^2/(4\pi\varepsilon_0) = 1 \).

- As a result, the operators will be written as follows from now on:

\[
\hat{T} \equiv -\frac{1}{2} \sum_{i=1}^{N} \nabla_{\mathbf{r}_i}^2 = -\frac{1}{2} \sum_{i=1}^{N} \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)
\]

\[
\hat{W}_{ee} \equiv \sum_{i<j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times
\]

\[
v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}.
\]
Nuclear potential energy (in atomic units) for a linear and periodic chain of atoms:

\[ v_{ne}(\mathbf{r}) \equiv v_{ne}(x, y, z) = -\sum_{n \in \mathbb{Z}} \frac{Z}{\sqrt{(x - na)^2 + y^2 + z^2}} = v_{ne}(x + a, y, z) \]

where \( \mathbb{Z} = \{0, \pm 1, \pm 2, \ldots\} \) and \( a \) is the lattice constant.

For simplicity, we will consider a chain of hydrogen atoms (\( Z = 1 \)) in the following.
Nuclear potential for $M$ hydrogen atoms and $a = 3.0$ a.u.
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Nuclear potential for $M$ hydrogen atoms and $a = 3.0$ a.u.

$M = 101$
In order to get some insight into the effect of a periodic nuclear potential on the wavefunction we will (for now) restrict the discussion to one-electron systems.

By analogy with chemistry, we can use, as a starting point, the concept of linear combination of atomic orbitals (LCAO).

Let’s start with a single atom at position $x = 0$:

$$\Psi_0(x) = \frac{1}{\sqrt{\pi}} e^{-|x|}$$
Bonding orbital in the diatomic ($M = 2$)

$$\Psi_0(x) = \frac{1}{\sqrt{2\pi}} \left( e^{-|x|} + e^{-|x-a|} \right) \text{ with } a = 3.0 \text{ a.u.}$$
Bonding/antibonding orbitals in the diatomic ($M = 2$)

$$\Psi_{\pm}(x) = \frac{1}{\sqrt{2\pi}} \left( e^{-|x|} \pm e^{-|x-a|} \right) \text{ with } a = 3.0 \text{ a.u.}$$

\[ \Psi_{+}, \Psi_{-} \]
Bonding/antibonding densities in the diatomic \((M = 2)\)

\[
\Psi_{\pm}(x) = \frac{1}{\sqrt{2\pi}} \left( e^{-|x| \pm e^{-|x-a|}} \right) \text{ with } a = 3.0 \text{ a.u.}
\]
\[ \Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n\times a|} \quad \text{where } a = 3.0 \text{ a.u.} \]
\[ \Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n \times a|} \quad \text{where } a = 3.0 \text{ a.u.} \]
\[ \Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n \times a|} \quad \text{where } a = 3.0 \text{ a.u.} \]

\[ n_0(x) = |\Psi_0(x)|^2 \]

\( M = 11 \)
\[ \Psi_0(x) = \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n \times a|} \quad \text{where } a = 3.0 \text{ a.u.} \]
Hückel (or tight-binding) model

- Let us try to rationalize our chemical approach from *first principles*.

- How can we generate (approximate) *solutions* to the Schrödinger equation?

- We can *project* the latter *onto a basis* of (localized) 1s atomic orbitals:

  \[ \phi_n(r) = \frac{1}{\sqrt{\pi}} e^{-\sqrt{(x-na)^2+y^2+z^2}} \]

- The (one-electron) Hamiltonian matrix elements are

  \[ h_{nm} = \langle \phi_n | \hat{h} | \phi_m \rangle = \int dr \ \phi^*_n(r) \times \hat{h} \phi_m(r), \]

  where \( \hat{h} \equiv -\frac{1}{2} \nabla^2_r + v_{ne}(r) \times \).
Hückel (or tight-binding) model

**EXERCISE** [solution available here]

(1) Show that the diagonal elements $h_{nn}$ have the same value (the “$\alpha$” of Hückel theory).

(2) Show that the matrix elements $h_{n(n+1)}$ between two neighboring 1s orbitals have the same value (the “$\beta$” of Hückel theory, also denoted “$t$” or “$-t$”).

(3) Show that, if we neglect the overlap between non-neighboring 1s orbitals in the calculation of the Hamiltonian matrix elements, then the latter can be written as follows,

$$ h_{nm} = \alpha \delta_{nm} + \beta \left( \delta_{n(m+1)} + \delta_{n(m-1)} \right) $$

*Comment 1*: for sake of simplicity, the overlap between neighboring orbitals is usually neglected when diagonalizing the one-electron Hamiltonian matrix. In other words, the orbital basis is assumed to be orthonormal.

*Comment 2*: $\alpha$ and $\beta$ are often used as parameters. They might be optimized in order to reproduce experimental data. In the latter case, they will also simulate (some part of) the effect of the two-electron repulsion.
Let us now return to the exact one-electron Schrödinger equation:

\[-\frac{1}{2} \nabla_r^2 \Psi(r) + v_{ne}(r) \times \Psi(r) = E \Psi(r)\]

The potential exhibits periodicity along the \(x\) axis (symmetry property):

\[v_{ne}(x + a, y, z) = v_{ne}(x, y, z)\]

We would like to transform the initial three-dimensional problem into the following one-dimensional one,

\[
\left[ -\frac{1}{2} \frac{d^2}{dx^2} + v(x) \times \right] \varphi(x) = \varepsilon \varphi(x)
\]

where \(v(x + a) = v(x)\).
EXERCISE

Let us consider the exact wavefunction separation

$$\Psi(r) \equiv \Psi(x, y, z) = \varphi_{yz}(x) \times \chi(x, y, z),$$

where the wavefunction $\varphi_{yz}(x)$, which is parameterized by the coordinates $y$ and $z$, fulfills the following one-dimensional Schrödinger equation,

$$\left[ -\frac{1}{2} \frac{d^2}{d x^2} + v_{yz}(x) \times \right] \varphi_{yz}(x) = \varepsilon_{yz} \varphi_{yz}(x) \quad \text{with} \quad v_{yz}(x) = v_{ne}(x, y, z).$$

Note that the above equation describes a one-dimensional periodic problem since $v_{yz}(x + a) = v_{yz}(x)$. 
(1) Show that the complementary wavefunction $\chi$ fulfills

\[
\left( -\frac{1}{2} \frac{\partial^2 \chi(x,y,z)}{\partial x^2} + \frac{1}{\varphi_{yz}(x)} \left[ -\frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} \right] (\varphi_{yz}(x) \chi(x,y,z)) \right) \\
- \frac{1}{\varphi_{yz}(x)} \frac{\partial \varphi_{yz}(x)}{\partial x} \frac{\partial \chi(x,y,z)}{\partial x} + \varepsilon_{yz} \times \chi(x,y,z) = E \chi(x,y,z).
\]

(2) Show that, if (i) we neglect the variation in both $y$ and $z$ of $\varphi_{yz}$, and (ii) $\chi$ does not vary with $x$, then the above equation becomes

\[
\left[ -\frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} \right] \chi(y,z) + \varepsilon_{yz} \times \chi(y,z) \approx E \chi(y,z).
\]
Periodicity in the wavefunction

- Our task is now to solve

\[
-\frac{1}{2} \frac{d^2}{dx^2} + v(x) \times \phi(x) = \epsilon \phi(x) \quad \text{where} \quad v(x + a) = v(x).
\]

- Let us warm up with the free particle problem \([v(x) = 0]\):

  (i) the solution reads \(\phi(x) = C \phi e^{ikx}\) and its energy \(\epsilon(k) = k^2/2\) is a function of \(k\).

  (ii) Note that \(\frac{1}{d^2 \epsilon(k)/dk^2} = 1\) is the mass of the electron in atomic units\(^*\).

  (iii) The variation of \(\epsilon(k)\) with \(k\), which will be modified by the nuclear potential, is referred to as the dispersion relation.

\(^*\) In SI units, \(\epsilon(k) = \frac{\hbar^2 k^2}{2m_e}\) thus leading to \(m_e^{-1} = \frac{1}{\hbar^2} \frac{d^2 \epsilon(k)}{dk^2}\).
In the presence of the atoms the wavefunction will have the more general form

\[ \varphi(x) = \int_{-\infty}^{+\infty} dk \ C_\varphi(k) e^{ikx} \]

The function \( C_\varphi(k) \) is the **Fourier transform** of the wavefunction \( \varphi \).

**Maths:** Note that \( \varphi(x) = 0 \ \forall x \Leftrightarrow C_\varphi(k) = 0 \ \forall k. \)
Periodicity in the wavefunction

**EXERCISE** that will be discussed during the exercise session.
[partial solution available here]

Let us introduce the Fourier transform of the nuclear potential:

\[ v(x) = \int_{-\infty}^{+\infty} dk \ C_v(k) \ e^{ikx} \]

(1) Show that the periodicity condition, \( v(x + a) = v(x) \ \forall x \), implies

\[ C_v(k) \left( 1 - e^{ika} \right) = 0 \ \forall k. \]

(2) Deduce that the potential can be written as

\[ v(x) = \sum_{K \in \frac{2\pi}{a} \mathbb{Z}} V_K e^{iKx} \equiv \sum_{m = -\infty}^{+\infty} C_v \left( \frac{2\pi m}{a} \right) e^{i \frac{2\pi m}{a} x}. \]

The ensemble of \( K \) values is called the **reciprocal lattice space**.
(3) Show, from the Fourier transform expressions of the potential and the wavefunction, that the Schrödinger equation can be rewritten as follows

\[
\left( \frac{k^2}{2} - \varepsilon \right) C_\varphi(k) + \sum_{K \in \frac{2\pi}{a} \mathbb{Z}} V_K C_\varphi(k - K) = 0, \quad \forall k \tag{1}
\]

or, equivalently \((k \to k - K')\),

\[
\left( \frac{(k - K')^2}{2} - \varepsilon \right) C_\varphi(k - K') + \sum_{K'' \in \frac{2\pi}{a} \mathbb{Z}} V_{(K'' - K')} C_\varphi(k - K'') = 0, \quad \forall k, \quad \forall K' \tag{2}
\]

(4) Check that the free-particle solutions are recovered from Eq. (1).
(5) Show that, if Eq. (2) is solved for a \textit{given and fixed} \( k \) value, it becomes equivalent to the following diagonalization problem

\[
H(k)X(k) = \varepsilon(k)X(k)
\]

(3)

where

\[
X(k) \equiv X_{K'}(k) = C\varphi(k - K')
\]

\[
H(k) \equiv H_{K'K''}(k) = \frac{(k - K')^2}{2}\delta_{K'K''} + V(K'' - K')
\]

(6) Eq. (3) has in principle an infinite number of solutions \( \left\{ X^{(n)}(k) \right\}_n \) with the corresponding energies \( \left\{ \varepsilon^{(n)}(k) \right\}_n \) where \( n \) is a quantum number. Show that the corresponding wavefunction reads

\[
\varphi^{(n)}(k, x) = \sum_{K' \in \frac{2\pi}{a} \mathbb{Z}} C^{(n)}_{\varphi}(k - K')e^{i(k-K')x}
\]
Periodicity in the wavefunction

(7) Bloch’s theorem states that the wavefunction can be written as follows,

\[ \varphi^{(n)}(k, x) = e^{ikx} \times u^{(n)}(k, x) \]

where \( u^{(n)}(k, x + a) = u^{(n)}(k, x) \leftarrow \text{periodicity of the lattice!} \)

Show that this theorem is indeed recovered from Eq. (4).

Let us recall our chemical approach:

\[ u^{(n)}(k, x) \leftarrow \lim_{M \to +\infty} \left( \frac{1}{\sqrt{\pi M}} \sum_{n=-(M-1)/2}^{(M-1)/2} e^{-|x+n \times a|} \right) \]

\[ e^{ikx} \xrightarrow{k=0} +1 \leftarrow \text{for any } x \ (\text{bonding!}) \]

\[ e^{ikx} \xrightarrow{k=2\pi/(Ma)} +1 \leftarrow \text{for } x = 0 \text{ and } e^{2i\pi/M} \text{ for } x = a \ (\text{antibonding if } M = 2) \]
One-electron picture of the many-electron problem

- The one-electron picture consists in (i) calculating the energy levels of a single electron and (ii) distributing all the electrons among them (Aufbau principle).

As you know, this picture does not give an exact description of the true electronic structure because of the two-electron repulsion. It becomes formally exact in Kohn–Sham DFT as, in this case, the one-electron picture reproduces the exact ground-state density.
More realistic band gaps from meta-generalized gradient approximations: Only in a generalized Kohn-Sham scheme

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FIG. 3. The band structure of Si calculated with PBE, gKS SCAN, and KS(KLI) SCAN.
Simplification of the *many-electron* problem

- The exact ground-state electronic structure is in principle described by a *many-electron wavefunction* $\Psi_0(x_1, x_2, \ldots, x_N)$.

- When it comes to describe an *extended system*, where the number of electrons $N$ may go to infinity, it is natural to wonder if the *wave function* is actually a well defined and reachable mathematical object.

- From a practical point of view, this is for sure *not the way to go*.

- State-of-the-art methods in condensed matter physics do not rely on many-electron wavefunctions.

- They use *reduced* quantities instead.

- The most famous one (in the physics community) is the time-ordered one-electron *Green function* $G(x, t_1; x', t_2)$.

- Another important (and simpler) quantity is the electron *density* $n(r) = -i \sum_{\sigma = \pm \frac{1}{2}} \lim_{t_2 \rightarrow t_1, t_1 < t_2} G(x, t_1; x, t_2)$, where $x \equiv (r, \sigma)$.

- The latter is the basic variable in *density-functional theory*. 
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = \]
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = -i\langle \Psi_0 | \hat{\Psi}(x, t_1)\hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

\[ |t_1 > t_2 \]
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = -i \langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

\[ i^2 = -1 \]

\[ |t_1 > t_2 \]
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = -i \langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

- Creates an electron at position/spin \( x' \) at time \( t_2 \)
- Removes an electron from position/spin \( x \) at time \( t_1 \)

\( t_1 > t_2 \)
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = -i \langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

- Creates an electron at position/spin \( x' \) at time \( t_2 \)
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\( t_1 > t_2 \)
The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = -i \langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

Creates an electron at position/spin \( x' \) at time \( t_2 \)

Electron affinity

\( t_1 > t_2 \)
The time-ordered one-electron Green function

\[
G(x, t_1; x', t_2) = \begin{cases} 
  i \langle \Psi_0 | \hat{\Psi}(x', t_2) \hat{\Psi}^\dagger(x, t_1) | \Psi_0 \rangle & \text{if } t_1 < t_2 \\
  -i \langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle & \text{if } t_1 > t_2 
\end{cases}
\]

Creates an electron at position/spin \(x'\) at time \(t_2\)

Electron affinity

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The time-ordered one-electron Green function

\[ G(x, t_1; x', t_2) = \pm i\langle \Psi_0 | \hat{\Psi}(x, t_1) \hat{\Psi}^\dagger(x', t_2) | \Psi_0 \rangle \]

- Creates an electron at position/spin \( x' \) at time \( t_2 \)
- Removes an electron from position/spin \( x \) at time \( t_1 \)

Electron affinity:
- \( t_1 > t_2 \)
- \( t_1 < t_2 \)
The time-ordered one-electron Green function

\[
-\hat{\Phi}(\mathbf{x}, t_1)\hat{\Phi}^\dagger(\mathbf{x}', t_2) \Psi(0) = \hat{\Phi}^\dagger(\mathbf{x}', t_2)\hat{\Phi}(\mathbf{x}, t_1) \Psi(0)
\]

- Creates an electron at position/spin \( \mathbf{x}' \) at time \( t_2 \)
- Removes an electron from position/spin \( \mathbf{x} \) at time \( t_1 \)

Electron affinity

\( t_1 > t_2 \)

Ionization

\( t_1 < t_2 \)
The time-ordered one-electron Green function

\[ G(x, t_1; x, t_2) = \]

\[ = i \langle \Psi_0 | \hat{\Psi}^\dagger(x, t_1) \hat{\Psi}(x, t_1) | \Psi_0 \rangle \]

If \( x = x' \) …
The time-ordered one-electron Green function

\[ G(x, t_1; x, t_2) = \]

\[ i \langle \Psi_0 | \hat{\Psi}^\dagger(x, t_1) \hat{\Psi}(x, t_1) | \Psi_0 \rangle = i \ n(x) \quad \text{Density!} \]