Some introductory notes on periodic Hartree-Fock

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This text gives a short technical exposition of what exactly we want to evaluate. It discusses (i) the form of the wave function and basis functions, (ii) Bloch waves, (iii) the relationship between super-cells, reciprocal-space grids (k-grids) and real-space translation grids (t-grids), and (iv) the general workings of a SCF program. Not covered are lattice sums: This text assumes short-range potentials.

I. UNIT CELL AND LATTICE VECTORS

Ultimately, we want to get the Hartree-Fock (HF) wave function of a three-dimensional periodic solid. For this we first need to define the periodic solid itself.

The solid is specified by the atomic configuration in the unit cell and the lattice vectors (which define how the unit cell is repeated in the three directions). The unit cell is defined by:

- The position of the atoms $\mathbf{R}_i$,
- their element number Z_i ($i = 1 \dots N_{\text{at}}$),
- any additional properties associated with the atoms (e.g., basis sets, effective core potentials).

This information is only specified for one cell. For example, for diamond, the unit cell would information on two carbon atoms.

The lattice itself is defined by three lattice vectors, $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$. The definition is such that for each atom i in the unit cell at position R_i, in the infinite solid there is another, equivalent atom at position

$$\mathbf{R}'_i = \mathbf{R}_i + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

for some combination of *integers* $n_1, \dots, n_3$. That is, the complete unit cell is repeated in each of the directions $\mathbf{a}_i$, an infinite number of times.

We combine the number of allowed displacements into a set of translation operators $T = (n_1^T, n_2^T, n_3^T)$, each of which is defined by

$$\hat{T}\mathbf{R}_i := \mathbf{R}_i + n_1^T\mathbf{a}_1 + n_2^T\mathbf{a}_2 + n_3^T\mathbf{a}_3.$$

II. WHAT IS THE MESSAGE OF THIS TEXT?

- A number of unit-cells is comined into super-cells. Basis functions within the super-cells are treated as independent degrees of freedom, even if they originate from the same basis function in the unit-cell. Super-cells are used to combat the *finite size error*, which can occur even in periodically symmetric wave functions. The set of translation vectors from the first unit cell to all other unit cells in a super-cell is denoted $\{\mathbf{T}_i; (i = 1 \dots N_u)\}$ (N_u: number of unit cells in the super-cell).
- The real-space basis functions we will ultimately use are periodic with the period of the super-cell size.
- Due to periodic symmetry, one-particle operators have the property that

  $$\forall T: \ \langle\mu|\hat{o}|\nu\rangle = \langle\hat{T}\mu|\hat{o}|\hat{T}\nu\rangle$$

  for all translation vectors T (in general: for all symmetry operations T of the system) and all basis functions μ, ν. As a consequence, the operator is fully specified (on the entire lattice), by the matrix elements $\langle\mu|\hat{o}|\hat{T}_i\nu\rangle$ for $\mu, \nu \in U$ (U: first unit cell) and $i = 1 \dots N_u$ the translations between the first unit cell and the other unit cells in the super-cell.

  Consequently, objects like Fock matrices, overlap matrices, etc. should be represented in a format

  ```
  nAo x nAo x nUnitCells
  ```

  where nAo is the number of basis functions in the unit cell, and nUnitDisp is the number of unit-cells in a super-cell (indexing the translation between the unit cell of μ and ν). Alternatively, μ can be thought of as being restricted to the first unit cell, and ν running over all unit cells.
- This symmetry is *very* easy to exploit in practice and should be considered from the very beginning. Note that full-supercell-basis matrices can be constructed trivially from this representation.
- The representation

  ```
  nAo x nAo x nUnitCells
  ```

  can be converted to a fully symmetry adapted basis *which has exactly the same size and produces exactly the same wave wave function* by a one-particle basis transformation. The new format is

  ```
  nAo x nAo x nGridK
  ```

  where nGridK is the number of k-space grid points (==number of unit cells in the supercell). The latter representation is favorable for matrix operations, because it block-diagonalized totally symmetric operators. But for the beginning we can ignore it.

  The k-space representation is not favorable compared to the real- space representation for assembling matrix elements of the Fock or other matrices.
- Two simple python programs are attached which demonstrate the finite size error and the conversion between the real-space and the momentum-space basis sets.

III. (BLOCH WAVES)

In a periodic system, the full Hamiltonian H commutes with all lattice translation operators:

$$\forall T: \ [H, T] = 0$$

Consequently, we can find a basis of the full system which diagonalizes H and a set of generator translations (displacements by the three lattice directions $\mathbf{a}_i$) at the same time. Due to this, we can restrict our search for eigenstates of H to eigenvectors which transform according to a given irreducible representation of the translation group. The translation irreps are labelled by $\mathbf{k}$ vectors. This also applies for Hartree-Fock wave functions.

Similarly, we can define a one-particle basis which consists of eigenvectors of all generators of the space group (in particular, the translation generators) at the same time.

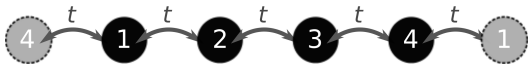
[!more on Bloch waves: Bloch waves are one-particle functions transforming according to a given $\mathbf{k}$ irrep.].

IV. FINITE SIZE EFFECTS VS PERIODIC BOUNDARY CONDITIONS—TIGHT BINDING

It must be stressed that there are two distinct problems in the treatment of periodic solids:

- Finite size effects (approximations to the flexibility of the wave function)
- And periodic boundary conditions (PBC; PBC is the process of making sure that our approximate wave function has periodic symmetry. The main problem is the evaluation of matrix elements of long-range interactions over periodically symmetric basis functions).

Imposing periodic boundary conditions (e.g., of the potentials) on an approximate wave function is *not* enough to eliminate finite size effects, even though in principle we compute a wave function for an infinite system. This is most easily seen in a one-dimensional tight-binding model (or Hueckel model), where imposing periodic boundary conditions is trivial:



with Hamiltonian (% is modulo):

$$H = -t \sum_r (a^\dagger_{(r+1)\%L} a_r + a^\dagger_r a_{(r+1)\%L}). \qquad (1)$$

That is: Our model consists of L sites which are explicitly treated before the entire system is repeated in both directions; there is a hopping term between the sites; and the $L+1$'th site and the 1-site are considered equivalent, as are the L'th site and the 0'th site. (In the previously established language, the unit cell would be a single site, and a lattice translation would be a translation by one site. Additionally, we define the explicitly treated region of L sites as a *supercell*, and the set of displacement vectors between a supercell and its (infinite number of) replicas as $\{\mathbf{S}\}$. Here, each $\mathbf{S}$ is a translation by $n \cdot L$ ($n \in \mathbb{Z}$) sites.) In matrix form the model's Hamiltonian is written as:

$$\mathbf{t} \equiv \begin{pmatrix} 0 & -t & 0 & 0 & \dots & 0 & -t \\ -t & 0 & -t & 0 & \dots & 0 & 0 \\ 0 & -t & 0 & -t & \dots & 0 & 0 \\ 0 & 0 & -t & 0 & \dots & 0 & 0 \\ \vdots & & & & \ddots & & \\ 0 & 0 & 0 & 0 & -t & 0 & -t \\ -t & 0 & 0 & 0 & 0 & -t & 0 \end{pmatrix} \qquad \text{(with PBC)}$$

There are no long range potentials: Any ground state wave function formed from the Hamiltonian will have periodic symmetry (in the absence of degeneracy). Nevertheless, if we calculate the band energy per site with increasing supercell size L, we get a slow convergence behavior (see Tab. I and `finite-size-tight-binding.py`).

L	E/site
2	-2.00000
4	-1.00000
6	-1.33333
8	-1.20711
10	-1.29443
12	-1.24402
16	-1.25683
20	-1.26275
24	-1.26596
30	-1.27557
38	-1.27469
∞	-1.27324

TABLE I. Band energy per site at half filling for the minimal tight-binding model defined by equation (1) ($t := 1$). See `finite-size-tight-binding.py`. The energy for $L = \infty$ is $-4/\pi$.

The reason why we do not get the exact energy with a small (or even minimal L) is that we effective put a restriction on the wave function expansion. We are *imposing* that

$$\forall n \in \mathbb{Z}: \ \mu(r + n \cdot L) = \mu(r)$$

for all basis functions μ and all sites r. Our basis functions are not really basis functions for the individual local sites, but rather the sites and all their periodic images at the same time! A supercell calculation with L explictly treated sites is thus eqvivalent to performing a variational calculation on the full lattice, but with a restricted set of L-translation symmetric basis functions. See Fig. 1.

However, we also see that as we increase the super-cell size L before imposing the periodicity, we do get a convergence to the infinite limit.

V. FINITE SIZE EFFECTS & SUPER-CELLS IN AN AB-INITIO TREATMENT

We have just seen that we can obtain periodic limits by employing a restricted set of local basis functions, which themselves are periodically symmetric: But not with the periodicity

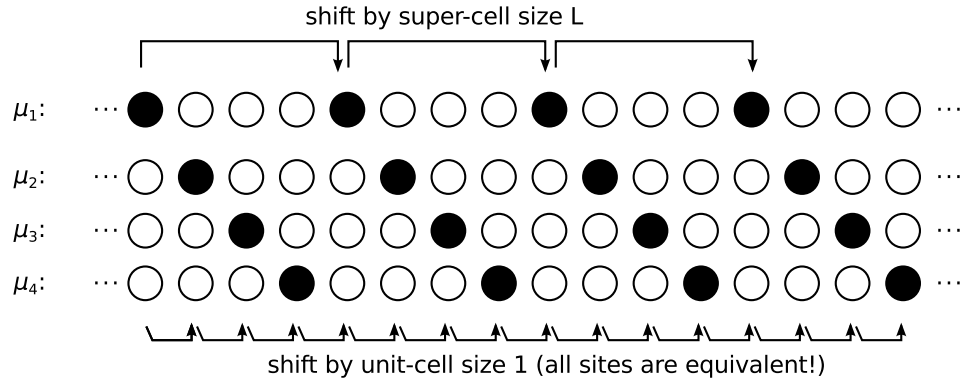


FIG. 1. Illustration of the periodic basis: A super-cell calculation with size $L = 4$ is eqvivalent to finding the HF ground state in the one-particle basis set spanned by the periodic basis functions $\mu_1, \ldots, \mu_4$. The period of the functions is the super-cell size L, not the unit-cell size 1. A linear combination of $\mu_1 \ldots \mu_4$ allows us to assign electrons to all sites on the lattice, but they are not independent.

of the lattice (i.e., translations by single unit cells), but the larger periodicity of the super-cell, L. In order to get a converged wave function, we will thus generally have to replicate our unit cell into the different space directions to form super-cells, and treat the resulting super-cell basis functions as independent, even if they originate from the same basis function in a unit cell (see Fig. 1); this happens in addition to to imposing periodic boundary conditions (with single unit-cell period) on potentials and/or operators.

This reasoning can also be applied to periodic symmetry on general wave functions in an ab initio treatment of solids: Instead of using raw Gaussian basis functions $\bar{\mu}(\mathbf{r})$, we will use Gaussian basis functions

$$\mu(\mathbf{r}) := \sum_{\mathbf{S}} \bar{\mu}(\mathbf{r} + \mathbf{S}) \tag{2}$$

where $\mathbf{S}$ runs over all displacements between two super-cells (that number is infinite) and $\bar{\mu}$ is a normal local Gaussian centered on one of the atoms of the super-cell (not the unit-cell). Like in the tight-binding case, we will normally be able to drop one of the summations from the basis functions to calculate matrix elements between different such periodic basis functions (more on that later).

VI. K-POINTS

The alternative to super-cell calculations is the usage of k-point symmetric basis functions; that is, basis functions which are symmetry- adapted to the translation group. Being symmetry adapted means that a basis function is an eigenfunction of the (unitary) translation operators. One can show that such an eigenfunction $\mu^{\mathbf{k}}(\mathbf{r})$ has the following property:

$$\mu^{\mathbf{k}}(\mathbf{r} + \mathbf{T}) = \exp(i\mathbf{k} \cdot \mathbf{T})\, \mu^{\mathbf{k}}(\mathbf{r}) \tag{3}$$

for all lattice translations (not super-cell translations!) $T = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ ($n_i \in \mathbb{Z}$), and some arbitrary fixed $\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$ ($k_i \in \mathbb{R}$). The $\mathbf{b}_1, \ldots, \mathbf{b}_3$ denote the *reciprocal space* basis vectors, and they are related to the lattice vectors $\mathbf{a}_1, \ldots, \mathbf{a}_3$ by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\det(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)} \qquad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\det(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)}$$
$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\det(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)}$$

(i.e., they are the bi-orthogonal basis to the $\mathbf{a}_1$,…,$\mathbf{a}_3$ vectors). It is sufficient to consider a restricted number of vectors in k-space (the first Brillouin zone), in the simplest case we only take vectors $\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3$ where $|k_i| \leq 1$ for all i.

In short: Any function which satisfies (3) for some $\mathbf{k}$ is symmetry adapted. The significance of this is that the Hamiltonian (and any other totally symmetric operator), is block-diagonal in $\mathbf{k}$-space. Matrix elements between basis functions belonging to different irreps (i.e., to different $\mathbf{k}$ vectors) vanish.

VII. ONE-PARTICLE TRANSFORMATIONS BETWEEN K-SPACE AND REAL-SPACE

Just like in real-space (infinite L), we cannot generally consider *all* possible basis functions in k-space, because there is an infinite number of them. We will thus have to choose a number of k points (a k-point grid). The calculation basis is then indexed by $(\widetilde{\mu}, \mathbf{k})$: an index $\widetilde{\mu}$ of a unit-cell-periodic basis function generated from a local basis function $\bar{\mu}$:

$$\widetilde{\mu}(\mathbf{r}) := \sum_{\mathbf{T}} \bar{\mu}(\mathbf{r} + \mathbf{T}) \tag{4}$$

(this differs from (4) by summing over lattice translations $\mathbf{T}$ instead of super-cell translations $\mathbf{S}$), and a vector $\mathbf{k}$ in reciprocal space. The actual function can be set to

$$\mu^{\mathbf{k}}(\mathbf{r}) := \exp(i\mathbf{k} \cdot \mathbf{r}) \sum_{\mathbf{T}} \bar{\mu}(\mathbf{r} + \mathbf{T}).$$

So what is the relationship between the super-cell basis and the k-point basis? The situation is: Under certain conditions, both basis sets can be made to span exactly the same space. And

then they can be seamlessly converted into each other. This is normally the case when a $N_1 \times N_2 \times N_3$ super-cell is used, and a regular $N_1 \times N_2 \times N_3$ k-point grid.

The attached file `1d-lattice-kgrid-vs-tgrid.py` demonstrates this for a one-dimensional example. It shows how a Hamiltonian matrix can be assembled in real space, how it can be reduced to nAo × nAo × nUnitCell form, how matrices and orbitals can be transformed between real-space and k-space, and how both approaches lead to identical results for the ground state. Additionally it points out some considerations on how matrices can be represented in both cases.

[…more later…]

[disclaimer: written in one go from mind and probably full of errors. Will be fixed later.]