PBC and LSDALTON

Crystalline solids can be described as ordered repetitions of atoms or groups of atoms. In an ideal crystal all repeating units are identical and they can be related to each other by the lattice vector

$$\mathbf{R}_n = u\mathbf{t}_1 + v\mathbf{t}_2 + w\mathbf{t}_3$$

u, v and $w \in \mathbb{Z}$

The set of all vectors $\mathbf{K}$ *that yield plane waves with the periodicity of a given lattice is known as its reciprocal lattice.*

$$e^{iK(r+R_n)} = e^{iKr}.$$

The reciprocal lattice can be generated by three primitive vectors $\mathbf{g}_i$ defined by the relation

$$\mathbf{t}_i \cdot \mathbf{g}_j = 2\pi\delta_{ij}.$$

Any vector in the reciprocal lattice can be written as a linear combination of the $\mathbf{g}_i$.

$$\mathbf{k} = \sum_{i=1}^{3} k_i \mathbf{g}_i.$$

The eigenfunctions to a periodic Hamiltonian are the so called Bloch functions

$$\psi_{\mu\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mu\mathbf{k}}(\mathbf{r}),$$

where $u_{\mu\mathbf{k}}(\mathbf{r})$ is periodic in $\mathbf{r}$. It is easy to see that the wavefunction has the property

$$\psi_{\mu\mathbf{k}}(\mathbf{r} + \mathbf{R}_n) = e^{i\mathbf{k}\mathbf{R}_n} \psi_{\mu\mathbf{k}}(\mathbf{r}).$$

The Schrödinger equation for a Bloch function gives us the so called band-energies, ie. energy levels, μ, that are dependent on the parameter k.

$$H\psi_{\mu\mathbf{k}} = \varepsilon_{\mu,k} \psi_{\mu\mathbf{k}}.$$

For the moment only closed shell HF is implemented.
The self consistent field equations have to be solved for each k value in the first Brillouin zone:

$$F(k)C(k) = \varepsilon(k)S(k)C(k)$$

The k dependency of the Fock matrix is given by the fourier transformation

$$F_{\mu\nu}(k) = \sum_{\mathbf{j}} e^{ikj} F^{0j}_{\mu\nu}, \tag{1}$$

where j is a lattice vector and

$$F^{0j}_{\mu\nu} = h^{0j}_{\mu\nu} + J^{0j}_{\mu\nu} + K^{0j}_{\mu\nu}. \tag{2}$$

Each part of the fock matrix has first to be computed in real space.

- The connection with LSDalton is in the computation of the integrals which are all done in realspace.
- In the pbc code we loop over all lattice cells that are necessary in the fourier transform, and call the integrals in LSDalton.

A pseudo-code for the kinetic energy:

```
DO index=1,num_latvectors
  call TYPEDEF_setmolecules(setting,refcell,1,&
 &                          latt_cell(index),3)

  call II_get_kinetic(lupri,luerr,setting,kin)
ENDDO
```