EXTENSION OF CIPSI and DMC(QMC) TO PERIODIC SOLIDS
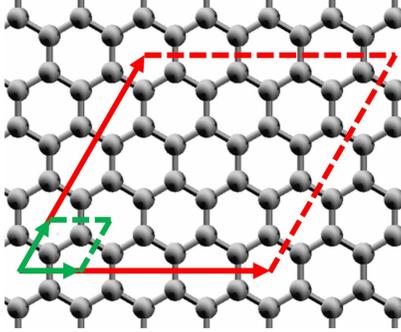
The simplest way to address the problem (**cluster approach**): To extract a **finite** piece of the infinite solid and treat it as a (big) molecule with Hamiltonian

$$H(N) = -\frac{1}{2} \sum_{i=1}^{n_{el}} \nabla_i^2 + \frac{1}{2} \sum_{i=1}^{n_{el}} \sum_{j=1}^{n_{el}}{}' \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i=1}^{n_{el}} \sum_{\alpha=1}^{n_{nuc}} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|}$$
$$+ \sum_{\alpha=1}^{n_{nuc}} \sum_{\beta=1}^{n_{nuc}}{}' \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \tag{1}$$

We are led back to the standard problem: Choose a gaussian basis set (GTO) and make a CIPSI calculation with QP and then DMC

Only NEW aspect: Results are evaluated for a finite N, the thermodynamic limit $N \to +\infty$ has to be taken. Said differently, the so-called **finite-size-effects (FSE)** are to be removed.

THE ONLY PROBLEM LEFT: REDUCE (DRASTICALLY) THE FSE

I) Periodize the external coulombic potential felt by the electrons

II) To massively save computational time: Rotate the GTO basis set to make it periodic

III) Play with the boundary conditions: Twist-Averaging

I) Periodize the external coulombic potential felt by the electrons

The Hamiltonian. The supercell Hamiltonian is of standard kinetic-plus-potential form, except that the one- and two-body coulombic potentials are now periodized to modelize the interaction of the electrons and nuclei of the supercell with the infinite set of the fixed charges corresponding to their periodic images

$$H(N) = -\frac{1}{2} \sum_{i=1}^{n_{el}} \nabla_i^2$$

$$+\frac{1}{2} \sum_{n_A,n_B,n_C} \sum_{i=1}^{n_{el}} \sideset{}{'}\sum_{j=1}^{n_{el}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j + n_A\mathbf{A} + n_B\mathbf{B} + n_C\mathbf{C}|}$$

$$-\sum_{n_A,n_B,n_C} \sum_{i=1}^{n_{el}} \sum_{\alpha=1}^{n_{nuc}} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha^0 + n_A\mathbf{A} + n_B\mathbf{B} + n_C\mathbf{C}|}$$

$$+\sum_{n_A,n_B,n_C} \sum_{\alpha=1}^{n_{nuc}} \sideset{}{'}\sum_{\beta=1}^{n_{nuc}} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta^0 + n_A\mathbf{A} + n_B\mathbf{B} + n_C\mathbf{C}|} \tag{2}$$

Ewald summation technique:

$$V(\mathbf{r}_1, ..., \mathbf{r}_n) = \frac{1}{2} \sum_{\mathbf{n}} \sum_{i=1}^{n} \sideset{}{'}\sum_{j=1}^{n} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|} \tag{3}$$

with $\mathbf{n} = (n_A, n_B, n_C)$ and $\mathbf{n}L = n_A\mathbf{A} + n_B\mathbf{B} + n_C\mathbf{C}$. Ewald summation enables to compute V as a sum of two contributions, a first one, short-ranged in real space, and, the other, short-ranged in reciprocal space. Both contributions are expressed as an infinite sum converging very rapidly (gaussian-like decrease of the general term), thus leading to a very fast and efficient calculation of the potential. To be more precise, the potential V is replaced by

$$V_E = \frac{1}{2} \sum_{\mathbf{n}} \sum_{i=1}^{n} \sideset{}{'}\sum_{j=1}^{n} \frac{q_i q_j}{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|} erfc\left(\frac{|\mathbf{r}_i - \mathbf{r}_j + \mathbf{n}L|}{\sqrt{2}\sigma}\right)$$

$$+\frac{2\pi}{\Omega} \sum_{\mathbf{k}\neq 0} \frac{e^{-\frac{\sigma^2 k^2}{2}}}{k^2} |S(\mathbf{k})|^2 - \frac{1}{\sqrt{2n}\sigma} \sum_{i=1}^{n} q_i^2 \tag{4}$$

II) To massively save computational time: Rotate the GTO basis set to make it periodic

The one-electron basis functions are chosen to be crystalline Gaussian-based atomic orbitals

$$\chi_{\mu\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{T}} e^{i\mathbf{k}\cdot\mathbf{T}} \tilde{\chi}_{\mu}(\mathbf{r} + \mathbf{T}), \tag{5}$$

i.e., the periodized (or translationally-symmetry-adapted) version of the (localized) Gaussian atomic orbitals $\tilde{\chi}_{\mu}(\mathbf{r})$ from the supercell.

The molecular orbitals of the system are then defined as

$$\phi_{p\mathbf{k}}(\mathbf{r}) = \sum_{\mu}^{N_{\text{bas}}} C_{\mu p}(\mathbf{k})\,\chi_{\mu\mathbf{k}}(\mathbf{r}), \tag{6}$$

where N_{bas} is the number of basis functions, and the molecular orbital coefficients $C_{\mu p}(\mathbf{k})$ are now momentum-dependent due to the translational-symmetry adaptation of the basis functions.

The only new aspect with respect to standard CI implementations is the use of complex-valued orbitals, integrals and Hamiltonian matrix elements. Let us denote the two-electron integrals as

$$* p\mathbf{k}_p q\mathbf{k}_q r\mathbf{k}_r s\mathbf{k}_s = \iint_{\Omega^2} d\mathbf{r}_1 d\mathbf{r}_2 \phi^*_{p\mathbf{k}_p}(\mathbf{r}_1)\phi^*_{q\mathbf{k}_q}(\mathbf{r}_2)\frac{1}{r_{12}}\phi_{r\mathbf{k}_r}(\mathbf{r}_1)\phi_{s\mathbf{k}_s}(\mathbf{r}_2). \tag{7}$$

Since the one-particle basis functions are invariant with respect to the primitive lattice translation vectors b, **the two-electron integrals must conserve crystal momentum**, *i.e.*, $\boxed{\mathbf{k}_p + \mathbf{k}_q = \mathbf{k}_r + \mathbf{k}_s + \mathbf{g}}$,

where $\mathbf{g}$ is a reciprocal lattice vector of the primitive cell.

III) Play with the boundary conditions: Twist-Averaging

Translating one electron of the supercell by a superlattice vector (say, $\mathbf{A} = L\mathbf{a}$) generates a phase factor, $e^{iL\mathbf{k}\cdot\mathbf{a}}$, for each of the orbitals of the CI determinants. Accordingly, a global phase factor common to all determinants is obtained whenever all these individual phase factors are made equal, that is

$$e^{iL\mathbf{k}_1\cdot\mathbf{a}} = e^{iL\mathbf{k}_2\cdot\mathbf{a}} = \ldots = e^{i\theta}, \tag{8}$$

where θ is some arbitrary angle (or twist) between $-\pi$ and π.

Boundary conditions can be varied with θ from $-\pi$ to $+\pi$, $\theta = 0$ and $\theta = \pm\pi$ corresponding to periodic and anti-periodic boundary conditions, respectively.

For a given system size, a property O can be computed by averaging out its values for different $\mathbf{K}$ values (or twists θ). In the limit of an infinite set of sampling values, we have

$$O = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\theta \Psi_\theta \hat{O} \Psi_\theta, \tag{9}$$

where Ψ_θ is the exact wavefunction of the system for the corresponding boundary condition.