# Ewald summation

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# The context

The HF orbitals are expanded in a Gaussian basis set ($i, \alpha$ are local indices of the supercell and **Q, P** are translation vectors of the lattice):

$$\psi_i^{\mathbf{P}}(\vec{r}) = \sum_{\alpha\mathbf{Q}} \phi_\alpha^{\mathbf{Q}}(\vec{r}) C_{\alpha\mathbf{Q};i\mathbf{P}} \tag{1}$$

The Coulomb energy is given by (with $P_{\gamma\delta}^{\mathbf{Q}} = \left(\mathbf{C}^\dagger\mathbf{C}\right)_{\gamma\mathbf{0};\delta\mathbf{Q}}$ ):

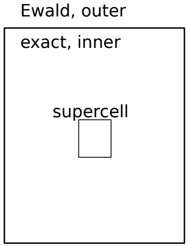
$$E_{Coul} = \frac{1}{2}\sum_{ij\mathbf{TP}} \int \frac{\psi_i^{\mathbf{P}}(\vec{r})\psi_i^{\mathbf{P}}(\vec{r})\psi_j^{\mathbf{T}}(\vec{r}')\psi_j^{\mathbf{T}}(\vec{r}')}{\mid \vec{r} - \vec{r}' \mid} d\vec{r}d\vec{r'} \tag{2}$$

$$\frac{E_{Coul}}{N} = \frac{1}{2}\sum_{\alpha\beta\mathbf{T}} P_{\alpha\beta}^{\mathbf{T}} \sum_{\gamma\delta\mathbf{Q}} P_{\gamma\delta}^{\mathbf{Q}} \sum_{\mathbf{S}} \left(\phi_\alpha^{\mathbf{0}}\phi_\beta^{\mathbf{T}} \mid \phi_\gamma^{\mathbf{S}}\phi_\delta^{\mathbf{S}+\mathbf{Q}}\right) \tag{3}$$

- For small $\mathbf{S}, \mathbf{T}, \mathbf{Q}$ the terms in the sum can be calculated exactly.
- For large **T** or **Q**, the integrals become negligible.
- For large **S**, there is no overlap between $\phi_\alpha^{\mathbf{0}}\phi_\beta^{\mathbf{T}}$ and $\phi_\gamma^{\mathbf{S}}\phi_\delta^{\mathbf{S}+\mathbf{Q}}$.

# How to deal with large **S**-terms

- Treat the N-N, N-e and direct e-e terms simultaneously in the outer region with an Ewald summation.
- Create grid $G1$ in the reference supercell & assign point charges $\{q_i\}$.
- $\{q_i\}$ in outer region generate a potential in the reference supercell.
- Potential in reference supercell is sampled on the same grid $G1$.
- I: Unit cell info, inner region definition, $G1$, $\{q_i\}$.
- O: Potential due to outer region sampled at $G1$ in the reference supercell.



# Ewald summation

$$W = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{\mid \vec{r}_i - \vec{r}_j \mid} \tag{4}$$

Periodic distribution, with $\vec{r}_i = \tau_\alpha + \mathbf{T}$, $\tau_{\alpha\beta} = \tau_\alpha - \tau_\beta$:

$$\frac{W}{N} = \sum_{\alpha\beta\mathbf{T}}' \frac{q_\alpha q_\beta erf\left(\frac{1}{2}\sqrt{\eta} \mid \tau_{\alpha\beta} + \mathbf{T} \mid\right)}{2 \mid \tau_{\alpha\beta} + \mathbf{T} \mid} + \sum_{\alpha\beta\mathbf{T}}' \frac{q_\alpha q_\beta erfc\left(\frac{1}{2}\sqrt{\eta} \mid \tau_{\alpha\beta} + \mathbf{T} \mid\right)}{2 \mid \tau_{\alpha\beta} + \mathbf{T} \mid} \tag{5}$$

$$\begin{aligned} \frac{W}{N} &= \sum_{\alpha\beta} \frac{q_\alpha q_\beta}{2} \left( \frac{4\pi}{\Omega} \sum_{\mathbf{G} \neq 0} \frac{e^{-i\mathbf{G}.\tau_{\alpha\beta}} e^{-G^2/\eta}}{G^2} - \delta_{\alpha\beta} \sqrt{\frac{\eta}{\pi}} \right. \\ &+ \left. \sum_{\mathbf{T}}' \frac{erfc\left(\frac{1}{2}\sqrt{\eta} \mid \tau_{\alpha\beta} + \mathbf{T} \mid\right)}{\mid \tau_{\alpha\beta} + \mathbf{T} \mid} \right) \end{aligned} \tag{6}$$

when supercell charge neutral, $\Omega$ the volume of the supercell, $\mathbf{G}$ the reciprocal lattice vectors