Ewald summation

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We omit factors 1/2 in front of all terms.

Let Γ be the unit cell of a periodic crystal, L be its lattice and L^* its reciprocal lattice. We want to compute the energy per unit cell

$$\int_{\Gamma\times\mathbb{R}^3} \rho(x)\rho(y)V(|x-y|)dxdy$$

when $V(r) = 1/r$, and $\rho = \rho_{\mathrm{n}} + \rho_{\mathrm{e}}$ is the total density of charge (modulo corrections to account for self-interaction of point charges, ie prime sums). This integral is not summable and therefore does not make sense. However, if $V(r) = e^{-\varepsilon r}/r$ is a Yukawa interaction with $\varepsilon > 0$, then the integral is summable, and it turns out that this has a well-defined limit as $\varepsilon \to 0$. The strategy is to evaluate the $\varepsilon \to 0$ by rewriting the terms in absolutely convergent integrals/sums. We consider here the DFT case of ρ_{n} as an array of point charges and ρ_{e} as a smooth function, but the formalism can be easily extended to e.g. Madelung constants (both positive and negative discrete charges).

1 Continuous ρ

We start by computing the $\varepsilon \to 0$ limit when $\rho = \sum_{G\in L^*} c_G e^{iGx}$ is a smooth density of charge:

$$\begin{aligned}
\int_{\mathbb{R}^3} \rho(y)V(|x-y|)dy &= \sum_{G\in L^*} c_G \int_{\mathbb{R}^3} e^{iGy} V(|x-y|)dy \\
&= \sum_{G\in L^*} c_G e^{iGx} \int_{\mathbb{R}^3} e^{-iG(x-y)} V(|x-y|)dy \\
&= \sum_{G\in L^*} c_G \hat{V}(G) e^{iGx}
\end{aligned}$$

and so

$$\begin{aligned}
\int_{\Gamma\times\mathbb{R}^3} \rho(x)\rho(y)V(|x-y|)dxdy &= |\Gamma| \sum_{G\in L^*} |c_G|^2 \hat{V}(G) \\
&= |\Gamma| \sum_{G\in L^*} |c_G|^2 \frac{4\pi}{|G|^2+\varepsilon^2}
\end{aligned}$$

We see that if ρ is not neutral, then the limit $\varepsilon \to 0$ diverge. Otherwise, it converges to $\sum_{G\in L^*} |c_G|^2 \frac{4\pi}{|G|^2}$.

If we want to compute $\int_{\Gamma\times\mathbb{R}^3} \rho(x)\rho(y)V(|x-y|) = \mathrm{Re} \int_{\Gamma\times\mathbb{R}^3} \overline{\rho(x)}\rho(y)V(|x-y|)$, the result is the same with $\mathrm{Re}(\overline{c_G(\rho)} c_G(\rho'))$ instead of $|c_G(\rho)|^2$.

2 Discrete ρ

Let Z_α, x_α be the charges and positions of the nuclei in the unit cell, $\rho_{\mathrm{n}} = \sum_\alpha Z_\alpha \delta_{x_\alpha}$ and ρ_{e} the electronic charge, with $\int_\Gamma \rho_{\mathrm{n}} + \rho_{\mathrm{e}} = 0$. We want to compute the total sum

$$\int_{\Gamma\times\mathbb{R}^3} \Big(\rho_{\mathrm{e}}(x)\rho_{\mathrm{e}}(y)V(|x-y|) + 2\rho_{\mathrm{e}}(x)\rho_{\mathrm{n}}(y)V(|x-y|)\Big)dxdy + {\sum_{R\in L}}' \sum_{\alpha,\beta} Z_\alpha Z_\beta V(|x_\alpha - x_\beta - R|)$$

where the prime indicates that we don't sum identical atoms.

Again, we will take V to be the Yukawa interaction and let $\varepsilon \to 0$ in the end. The first two terms can be computed as before, with a divergence when $\varepsilon \to 0$ because of non-neutrality. For the third term, we cannot use the formalism above for the third term because the charge density is not smooth and so the real-space sum is not convergent. We split the Yukawa potential into two parts: a short-range $V_{\mathrm{sr},\varepsilon} = V_{\mathrm{sr}}(r)e^{-\varepsilon r}$, and a long-range $V_{\mathrm{lr},\varepsilon} = V_{\mathrm{lr}}(r)e^{-\varepsilon r}$.

For the long-range part, we want to drop the prime in the summation, but $V_{\mathrm{lr},\varepsilon}(0) = V_{\mathrm{lr}}(0) \neq 0$, and so

$$\begin{aligned}
\sum_{R\in L}{}' \sum_{\alpha,\beta} Z_\alpha Z_\beta V_{\mathrm{lr},\varepsilon}(|x_\alpha - x_\beta - R|) &= \sum_{R\in L}\sum_{\alpha,\beta} Z_\alpha Z_\beta V_{\mathrm{lr},\varepsilon}(|x_\alpha - x_\beta - R|) - \sum_\alpha Z_\alpha^2 V_{\mathrm{lr}}(0) \\
&= \int_{\Gamma\times\mathbb{R}^3} \rho_{\mathrm{n}}(x)\rho_{\mathrm{n}}(y) V_{\mathrm{lr},\varepsilon}(|x-y|)dxdy - \sum_\alpha Z_\alpha^2 V_{\mathrm{lr}}(0) \\
&= |\Gamma| \sum_{G\in L^*} |c_G(\rho_{\mathrm{n}})|^2 \hat{V}_{\mathrm{lr},\varepsilon}(G) - \sum_\alpha Z_\alpha^2 V_{\mathrm{lr}}(0)
\end{aligned}$$

(we have extended the formalism of section 1 to the case of smooth interaction of periodic distributions)

The $\varepsilon \to 0$ limit carries through without difficulty for all terms except the $G = 0$ terms. Collecting them all, we get, if $Z = \sum_\alpha Z_\alpha = -\int_\Gamma \rho_{\mathrm{e}}$,

$$\frac{1}{|\Gamma|}\left((Z^2 - 2Z^2)\frac{4\pi}{\varepsilon^2} + Z^2 \hat{V}_{\mathrm{lr},\varepsilon}(0)\right) = \frac{Z^2}{|\Gamma|}\left(\hat{V}_{\mathrm{lr},\varepsilon}(0) - \frac{4\pi}{\varepsilon^2}\right)$$

which must have a convergent limit as $\varepsilon \to 0$ because V_{lr} is assumed to capture the long-range Coulomb interaction.

We finally arrive at the final total energy

$$\begin{aligned}
&D(\rho_{\mathrm{e}},\rho_{\mathrm{e}}) + 2D(\rho_{\mathrm{e}},\rho_{\mathrm{n}}) + D_{\mathrm{lr}}(\rho_{\mathrm{n}},\rho_{\mathrm{n}}) + \sum_{R\in L}{}'\sum_{\alpha,\beta} Z_\alpha Z_\beta V_{\mathrm{sr}}(|x_\alpha - x_\beta - R|) \\
&- \sum_\alpha Z_\alpha^2 V_{\mathrm{lr}}(0) + \frac{Z^2}{|\Gamma|}\lim_{\varepsilon\to 0}\left(\hat{V}_{\mathrm{lr},\varepsilon}(0) - \frac{4\pi}{\varepsilon^2}\right)
\end{aligned}$$

where

$$\begin{aligned}
D(\rho,\rho') &= |\Gamma| \sum_{G\neq 0} \mathrm{Re}(\overline{c_G(\rho)}c_G(\rho'))\frac{4\pi}{|G|^2} \\
D_{\mathrm{lr}}(\rho,\rho') &= |\Gamma| \sum_{G\neq 0} \mathrm{Re}(\overline{c_G(\rho)}c_G(\rho'))\hat{V}_{\mathrm{lr}}(G)
\end{aligned}$$

Note that when electrons are considered discrete and we are computing a purely discrete sum, as in e.g. Madelung constants, the last term does not appear (because $Z = 0$).

3 Erf based splitting

Ewald summation employs a particular form of the short- and long-range splitting, based on the error function:

$$V(r) = \frac{1}{r} = \frac{\mathrm{erfc}(\eta r)}{r} + \frac{\mathrm{erf}(\eta r)}{r} = V_{\mathrm{sr}}(r) + V_{\mathrm{lr}}(r).$$

We have

$$\hat{V}_{\mathrm{lr},\varepsilon}(0) = \int_{\mathbb{R}^3} \frac{\mathrm{erf}(\eta r)}{r} e^{-\varepsilon r} dr = 4\pi \int_0^\infty r\,\mathrm{erf}(\eta r)\, e^{-\varepsilon r} dr = \frac{4\pi}{\eta^2}\int_0^\infty r\,\mathrm{erf}(r)\, e^{-\varepsilon r/\eta} = \frac{4\pi}{\eta^2} I(\varepsilon/\eta)$$

with

$$I(\alpha) = \int_0^\infty r\,\mathrm{erf}(r)\, e^{-\alpha r} dr$$

Numerically (TODO check with Mathematica), $I(\alpha) = \frac{1}{\alpha^2} - \frac{1}{4} + O(\alpha)$, so

$$\hat{V}_{\mathrm{lr},\varepsilon}(0) = \frac{4\pi}{\varepsilon^2} - \frac{\pi}{\eta^2} + O(\varepsilon)$$

and

$$\lim_{\varepsilon \to 0} \left(\hat{V}_{\mathrm{lr},\varepsilon}(0) - \frac{4\pi}{\varepsilon^2} \right) = -\frac{\pi}{\eta^2}$$

The Fourier transform of V_{lr} is obtained by noting that V_{lr} is the potential created by a Gaussian charge distribution:

$$\begin{aligned} \Delta V_{\mathrm{lr}} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \frac{\mathrm{erf}(\eta r)}{r} \right) = -\frac{4\eta^3}{\sqrt{\pi}} e^{-\eta^2 r^2} \\ \hat{V}_{\mathrm{lr}}(q) &= \frac{4\pi e^{-\frac{|q|^2}{4\eta^2}}}{|q|^2} \end{aligned}$$

This also gives an alternative derivation of Ewald summation, by writing $\rho_{\mathrm{n}} = \rho_{\mathrm{n}} - \rho_{\mathrm{n}} * G + \rho_{\mathrm{n}} * G$, where G is an appropriate Gaussian. The first two terms contribute a short-range potential, the last a long-range potential.

We get for the final expression

$$\begin{aligned} & D(\rho_{\mathrm{e}}, \rho_{\mathrm{e}}) + 2D(\rho_{\mathrm{e}}, \rho_{\mathrm{n}}) + D_{\mathrm{lr}}(\rho_{\mathrm{n}}, \rho_{\mathrm{n}}) + \sum_{R \in L}{}' \sum_{\alpha,\beta} Z_\alpha Z_\beta V_{\mathrm{sr}}(|x_\alpha - x_\beta - R|) \\ & - \frac{2\eta}{\sqrt{\pi}} \sum_\alpha Z_\alpha^2 - \frac{\pi Z^2}{|\Gamma| \eta^2} \end{aligned}$$

with

$$\begin{aligned} D(\rho, \rho') &= |\Gamma| \sum_{G \neq 0} \mathrm{Re}(\overline{c_G(\rho)} c_G(\rho')) \frac{4\pi}{|G|^2} \\ D_{\mathrm{lr}}(\rho, \rho') &= |\Gamma| \sum_{G \neq 0} \mathrm{Re}(\overline{c_G(\rho)} c_G(\rho')) \frac{4\pi e^{-\frac{|G|^2}{4\eta^2}}}{|G|^2} \end{aligned}$$