Mathematics 29: Madelung and Ewald

The Ewald technique is a clever *practical* method of performing lattice sums. Perhaps the simplest type of applicable lattice sum is an *electrostatic* or *Madelung* energy: One considers the cost of removing a charge from a neutral crystal:

$$E_j = \sum_{i \neq j} \frac{q_j q_i}{\mid \mathbf{R}_i - \mathbf{R}_j \mid}$$

where there are an array of charges of size q_i at positions $\mathbf{R}_i$, and we are removing the atom at position $\mathbf{R}_j$. This lattice sum is rather pathological mathematically, if the crystal has a homogeneous charge then this energy diverges, because:

$$\int_{S(R)} d^3\mathbf{r} \frac{\rho}{\mid \mathbf{r} \mid} \mapsto 2\pi\rho R^2$$

where $S(R)$ is a sphere. If we consider only a surface charge, then the energy *still* diverges because:

$$\int_{S(R)} \mid d^2\mathbf{S} \mid \frac{\sigma}{\mid \mathbf{r} \mid} \mapsto 4\pi\sigma R$$

In mathematical language, the sum is *not* absolutely convergent and depends non-trivially on the *order* in which terms are included. Since, at any finite range of summation, the eventual answer may be overturned by an as yet unnoticed surface charge, the convergence in any direct summation technique is necessarily appalling. The Ewald technique is a method for forcing the charge neutrality at infinity as an assumption and thereby improving the convergence of the summation.

The physical idea is to use the *fourier transform*: Properties which are long-range in real-space become short-range in reciprocal-space and vice-versa. The long-range poorly convergent real-space summation is taken over into reciprocal-space, but the short-range real-space summation is left behind, since if it were taken into reciprocal-space it would be poorly convergent at long-range there. The technique involves splitting up the original function into two pieces: One being quickly convergent in real-space and the other being quickly convergent in reciprocal-space. The summation is then performed in *both* spaces. Unfortunately, there are infinitely many ways to split up the function and so we need a guiding *principle*. Before we consider this physical issue, we first generate some mathematical facts.

The entire analysis stems from a consideration of the function:

$$S(x) = \lim_{N \mapsto \infty} S_N(x) \qquad S_N(x) = \sum_{n=-N}^{N} e^{inx} = \frac{\sin\left(N + \frac{1}{2}\right)x}{\sin\frac{x}{2}}$$

Considered as a *distribution*, we can establish its properties by integration with an infinitely differentiable compactly supported function, $f(x)$ say:

$$\int_\alpha^\beta dx \frac{\sin\left(N + \frac{1}{2}\right)x}{\sin\frac{x}{2}} f(x) = \left[(-1)\frac{\cos\left(N + \frac{1}{2}\right)x}{\left(N + \frac{1}{2}\right)}\frac{f(x)}{\sin\frac{x}{2}}\right]_\alpha^\beta + \int_\alpha^\beta dx \frac{\cos\left(N + \frac{1}{2}\right)x}{\left(N + \frac{1}{2}\right)}\frac{\partial}{\partial x}\left[\frac{f(x)}{\sin\frac{x}{2}}\right]$$

which tends to zero *provided* that none of the zeroes of $\sin\frac{x}{2}$ reside in the interval (α,β). We may therefore deduce that the function $S(x)$ vanishes everywhere except at the zeroes of $\sin\frac{x}{2}$, where there may be δ-functions. Since:

$$S_N(x+2\pi) = S_N(x)$$

we need only consider the contribution from the origin. To assess whether or not we have a δ-function at the origin, we need to consider:

$$\int_{-\eta}^{\eta} dx \frac{\sin\left(N+\frac{1}{2}\right)x}{\sin\frac{x}{2}} f(x) = \int_{-\eta\left(N+\frac{1}{2}\right)}^{\eta\left(N+\frac{1}{2}\right)} dz \frac{\sin z}{\left(N+\frac{1}{2}\right)\sin\frac{z}{2\left(N+\frac{1}{2}\right)}} f\left(\frac{z}{\left(N+\frac{1}{2}\right)}\right)$$

for small η. Taking the limit $N \mapsto \infty$ *carefully* leads quite naturally to:

$$\int_{-\eta}^{\eta} dx S(x) f(x) = \int_{-\infty}^{\infty} dz \frac{2\sin z}{z} f(0) \mapsto 2\pi f(0)$$

and hence:

$$S(x) = \sum_{n=-\infty}^{\infty} e^{inx} = 2\pi \sum_{m=-\infty}^{\infty} \delta(x-2\pi m)$$

This is the one-dimensional result from which we now generate a three-dimensional result. We need first to describe the real- and reciprocal-lattice:

$$\mathbf{R}(\mathbf{n}) = n_1\mathbf{R}_1 + n_2\mathbf{R}_2 + n_3\mathbf{R}_3 \qquad \mathbf{G}(\mathbf{n}) = n_1\mathbf{G}_1 + n_2\mathbf{G}_2 + n_3\mathbf{G}_3$$

in terms of three minimal periods, $\mathbf{R}_i$, integers $\mathbf{n} \equiv (n_1, n_2, n_3)$ and reciprocal lattice periods:

$$\mathbf{G}_1 = 2\pi\frac{\mathbf{R}_2\times\mathbf{R}_3}{V(\Omega)} \qquad \mathbf{G}_2 = 2\pi\frac{\mathbf{R}_3\times\mathbf{R}_1}{V(\Omega)} \qquad \mathbf{G}_3 = 2\pi\frac{\mathbf{R}_1\times\mathbf{R}_2}{V(\Omega)}$$

which are the unique vectors which satisfy:

$$\mathbf{R}_i.\mathbf{G}_j = 2\pi\delta_{ij}$$

provided that:

$$V(\Omega) = \mathbf{R}_1.(\mathbf{R}_2\times\mathbf{R}_3)$$

is the unit-cell volume, and the associated reciprocal space volume satisfies:

$$\tilde{V}(\tilde{\Omega}) = \mathbf{G}_1.(\mathbf{G}_2\times\mathbf{G}_3) = \frac{(2\pi)^3}{V(\Omega)}$$

The three-dimensional result may now be generated using the $\mathbf{G}_i$'s as a basis for reciprocal-space:

$$\mathbf{x} = z_1\mathbf{G}_1 + z_2\mathbf{G}_2 + z_3\mathbf{G}_3$$

and then:

$$\sum_{\mathbf{m}} e^{i(m_1\mathbf{R}_1+m_2\mathbf{R}_2+m_3\mathbf{R}_3).\mathbf{x}} = (2\pi)^3 \sum_{\mathbf{n}} \delta(\mathbf{x}.\mathbf{R}_1 - 2\pi n_1)\delta(\mathbf{x}.\mathbf{R}_2 - 2\pi n_2)\delta(\mathbf{x}.\mathbf{R}_3 - 2\pi n_3)$$

$$\mapsto (2\pi)^3 \sum_{\mathbf{n}} \delta^3(2\pi\mathbf{z} - 2\pi\mathbf{n}) = \sum_{\mathbf{n}} \delta^3(\mathbf{z} - \mathbf{n})$$

where we have used the one-dimensional result three times over and have employed our reciprocal-space basis. We complete the proof by returning to using $\mathbf{x}$ as our basis via the Jacobian:

$$\frac{\partial[\mathbf{x}]}{\partial[\mathbf{z}]} = \tilde{V}(\tilde{\Omega})$$

and then the final result is:

$$\sum_{\mathbf{m}} e^{i\mathbf{R}(\mathbf{m}).\mathbf{x}} = \tilde{V}(\tilde{\Omega}) \sum_{\mathbf{n}} \delta^3 \left[\mathbf{x} - \mathbf{G}(\mathbf{n})\right]$$

This is the main mathematical result employed in Ewald's technique, since it transfers a real-space lattice sum to a reciprocal-space lattice sum. The next step is to apply this result to a fourier transform.

We elect to define fourier transforms with the normalisation:

$$\tilde{f}(\mathbf{q}) = \int d^3\mathbf{r} e^{-i\mathbf{q}.\mathbf{r}} f(\mathbf{r}) \qquad f(\mathbf{r}) = \int \frac{d^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}.\mathbf{r}} \tilde{f}(\mathbf{q})$$

and then the fourier transform lattice sum becomes:

$$\sum_{\mathbf{m}} f(\mathbf{R}(\mathbf{m})) = \sum_{\mathbf{m}} \int \frac{d^3\mathbf{q}}{(2\pi)^3} e^{i\mathbf{q}.\mathbf{R}(\mathbf{m})} \tilde{f}(\mathbf{q}) \mapsto \frac{\tilde{V}(\tilde{\Omega})}{(2\pi)^3} \int d^3\mathbf{q} \tilde{f}(\mathbf{q}) \sum_{\mathbf{n}} \delta^3 \left[\mathbf{q} - \mathbf{G}(\mathbf{n})\right]$$

and so generically:

$$\sum_{\mathbf{m}} f(\mathbf{R}(\mathbf{m})) = \frac{1}{V(\Omega)} \sum_{\mathbf{n}} \tilde{f}(\mathbf{G}(\mathbf{n}))$$

where we have used the relationship between cell volumes.

The physical problem of current interest involves a *crystal* and hence an underlying crystal periodicity. Including the possibilities of including several atoms per unit cell, and the cunning trick of using a *phase* to provide different charges and establish a larger periodicity than actually exists, we are led to the quantity:

$$I_\beta = \sum_{\mathbf{m}\alpha}{}' \frac{q_\alpha q_\beta \cos\left[\mathbf{Q}.(\mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid}$$

where $\mathbf{c}_\alpha$ mark the positions of the atoms in the unit cell, q_α are the charges associated with the atoms, $\mathbf{Q}$ is the cunning phase usually employed in the absence of the sublattice degrees of freedom, and the contribution coming from the 'self-interaction' of the atom with itself is *omitted* from the summation as indicated by the prime. To apply the Ewald technique, we need to split the summation into two terms, one in real-space and the other in reciprocal-space. We employ the general split of:

$$1 = P(r) + Q(r)$$

with $Q(r)$ to be the real-space portion and $P(r)$ to be the reciprocal-space portion. It is necessary that $P(0) = 0$ in order to avoid carrying a divergent contribution across into reciprocal-space. We then repartition the summation into:

$$I_\beta = \sum_{\mathbf{m}\alpha}{}' \frac{q_\alpha q_\beta \cos\left[\mathbf{Q}.(\mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid} Q(\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid) - q_\beta^2 \frac{dP}{dr}(0)$$

$$+ \sum_{\mathbf{m}\alpha} \frac{q_\alpha q_\beta \cos\left[\mathbf{Q}.(\mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid} P(\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid)$$

where we have extracted out the term at the origin in the second contribution in order to use our lattice summation result. The quantity that we require to fourier transform is:

$$f_\beta(\mathbf{r}) = Re \sum_\alpha \frac{q_\alpha q_\beta \exp i\left[\mathbf{Q}.(\mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid} P(\mid \mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid)$$

which provides:

$$\tilde{f}_\beta(\mathbf{q}) = Re \int d^3\mathbf{r} e^{-i\mathbf{q}.\mathbf{r}} \sum_\alpha \frac{q_\alpha q_\beta \exp i\left[\mathbf{Q}.(\mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid} P(\mid \mathbf{r} + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid)$$

$$= \sum_\alpha q_\alpha q_\beta \cos \mathbf{q}.(\mathbf{c}_\alpha - \mathbf{c}_\beta) \int d^3\mathbf{s} e^{i\mathbf{s}.(\mathbf{Q}-\mathbf{q})} \frac{P(\mid \mathbf{s} \mid)}{\mid \mathbf{s} \mid}$$

and we have used the fact that $P(r)$ is real and that the integral is inversion symmetric. The final integral may be manipulated into the form:

$$\int d^3\mathbf{s} e^{i\mathbf{s}.(\mathbf{Q}-\mathbf{q})} \frac{P(\mid \mathbf{s} \mid)}{\mid \mathbf{s} \mid} = 4\pi \int_0^\infty ds P(s) \frac{\sin s \mid \mathbf{Q} - \mathbf{q} \mid}{\mid \mathbf{Q} - \mathbf{q} \mid}$$

and the integrating by parts and using $P(0) = 0$:

$$= \frac{4\pi}{\mid \mathbf{Q} - \mathbf{q} \mid^2} \int_0^\infty ds \cos s \mid \mathbf{Q} - \mathbf{q} \mid \frac{dP}{ds}(s)$$

and the final result becomes:

$$I_\beta = \sum_{\mathbf{m}\alpha}{}' \frac{q_\alpha q_\beta \cos\left[\mathbf{Q}.(\mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta)\right]}{\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid} Q(\mid \mathbf{R}(\mathbf{m}) + \mathbf{c}_\alpha - \mathbf{c}_\beta \mid) - q_\beta^2 \frac{dP}{dr}(0)$$

$$+ \frac{1}{V(\Omega)} \sum_{\mathbf{n}} \sum_\alpha q_\alpha q_\beta \cos \mathbf{G}(\mathbf{n}).(\mathbf{c}_\alpha - \mathbf{c}_\beta) \frac{4\pi}{\mid \mathbf{G}(\mathbf{n}) + \mathbf{Q} \mid^2} \int_0^\infty ds \cos s \mid \mathbf{G}(\mathbf{n}) + \mathbf{Q} \mid \frac{dP}{ds}(s)$$

for an arbitrary splitting $P(r) + Q(r) = 1$ and $P(0) = 0$.

We now arrive at the important physical decision as to how to choose this splitting into real- and reciprocal-space parts: We employ a choice which is defined by *two* fundamental ideas: Often it is very valuable to have the summation restricted to only one of the two spaces, but *still* be strongly convergent. Since the function is only

evaluated at reciprocal lattice sites, we can make any real-space modification up to the first such vector without interfering with the real-space summation. We elect to *cut-off* the real-space contribution at a finite radius, R_0 say, beyond which $Q(r)$ vanishes. If R_0 is chosen to be smaller than the smallest non-zero lattice vector, then the real-space sum *vanishes*. This is particularly useful when the real-space function is a two- or three-site integral, where the case $\mathbf{R} = \mathbf{0}$ may be performed due to the extra symmetry but the other cases are numerically very intensive. For this case, the reciprocal space contribution dominates at long-range in real-space, and we find $P(r) = 1$ when $r > R_0$. Since the derivative vanishes, we find that the relevant quantity reduces to:

$$\tilde{P}(x) = \int_0^{R_0} ds \cos sx \frac{dP}{ds}(s)$$

Our final task is to try to ensure that $\tilde{P}(x)$ decays relatively fast in reciprocal-space. If the function $P(s)$ is *smooth*, then its fourier transform decays fast at infinity. For a general function, the idea is encapsulated by:

$$\int ds e^{isx} P(s) = \int ds e^{isx} \left[\frac{i}{x}\right]^n \frac{d^n P}{ds^n}(s)$$

provided that no boundary effects are encountered and that no singularities are picked up by the differentiation, ie that $P(s)$ is *smooth*. For the current case, we need to ensure that $P(s)$ is smooth at the edges of the integration region, $(0, R_0)$. This is accomplished by forcing:

$$\frac{dP_n}{dr}(r) = \frac{1}{N_n} r^n (R_0 - r)^n$$

and choosing the normalisation, N_n, so that:

$$\int_0^{R_0} dr \frac{dP_n}{dr} = P_n(R_0) - P_n(0) = 1$$

as required by continuity. This corresponds to:

$$N_n = \int_0^{R_0} dr r^n (R_0 - r)^n = \left[\frac{R_0}{2}\right]^{2n+1} \int_{-1}^{1} du (1-u^2)^n = \left[\frac{R_0}{2}\right]^{2n+1} \frac{2^{2n+1} n! n!}{(2n+1)!}$$

where we have introduced the new variable $2r = R_0(1+u)$ which rescales the integration region. In terms of this new variable:

$$\frac{R_0}{2} \frac{dP_n}{dr}\left(\frac{R_0}{2}(1+u)\right) = \frac{(2n+1)!}{2^{2n+1} n! n!} (1-u^2)^n$$

and so the quantities of fundamental interest are:

$$P_n(r) = \frac{(2n+1)!}{2^{2n+1} n! n!} \int_{-1}^{\frac{2r}{R_0}-1} du (1-u^2)^n \theta(1-u)$$

$$Q_n(r) = \frac{(2n+1)!}{2^{2n+1} n! n!} \int_{\frac{2r}{R_0}-1}^{1} du (1-u^2)^n \theta(R_0 - r)$$

in real-space and:

$$\tilde{P}_n(x) = \frac{(2n+1)!}{2^{2n+1}n!n!} Re \int_{-1}^{1} du(1-u^2)^n \exp i \left[\frac{R_0 x}{2}(1+u)\right]$$

$$= \cos\left[\frac{R_0 x}{2}\right] \frac{(2n+1)!}{2^{2n+1}n!n!} \int_{-1}^{1} du(1-u^2)^n \exp i \left[\frac{R_0 x}{2} u\right]$$

in reciprocal-space.

At this juncture it is useful to rationalise our chosen splitting, by extracting out the constants and simple quantities in the definitions:

$$Q_n(x) = q_n\left(\frac{2x}{R_0} - 1\right) \qquad \tilde{P}_n(x) = \cos\left(\frac{R_0 x}{2}\right) p_n\left(\frac{R_0 x}{2}\right)$$

where:

$$q_n(z) = \frac{(2n+1)!}{2^{2n+1}n!n!} \int_z^1 du(1-u^2)^n \theta(1-z^2)$$

$$p_n(z) = \frac{(2n+1)!}{2^{2n+1}n!n!} \int_{-1}^{1} du(1-u^2)^n e^{izu}$$

Integration by parts provides a useful recurrence relationship for the $q_n(z)$:

$$q_n(z) = q_{n-1}(z) - \frac{(2n)!}{2^{2n+1}n!n!} z(1-z^2)^n$$

but the reciprocal-space quantities are more subtle. Integration by parts provides:

$$p_n(z) = (-1)(2n+1)\frac{1}{z}\frac{d}{dz} p_{n-1}(z)$$

and hence by iteration:

$$p_n(z) = (-1)^n \frac{(2n+1)!}{2^n n!} \left[\frac{1}{z}\frac{d}{dz}\right]^n \frac{\sin z}{z}$$

which are directly related to the so-called spherical Bessel's functions. Employing the operator:

$$D = \frac{1}{z}\frac{d}{dz}$$

it is easy to verify that:

$$(z^2 D^2 + 3D + 1)p_0(z) = 0$$

and hence that:

$$(z^2 D^n + (2n-1)D^{n-1} + D^{n-2})p_0(z) = 0$$

which is a form of recurrence relationship:

$$p_n(z) = \frac{4n^2 - 1}{z^2}\left[p_{n-1}(z) - p_{n-2}(z)\right]$$

Although the quantities $q_n(z)$ are easy to calculate, these $p_n(z)$ are a lot more difficult, and it is useful to have a Taylor's expansion:

$$p_n(z) = \sum_{r=0}^{\infty} \frac{(2n+1)!(n+r)!}{(2n+2r+1)!r!n!}(-1)^r z^{2r}$$

Under the current assumptions our Ewald technique reduces to:

$$I_\beta = \sum_{\mathbf{R}\alpha}{}' \frac{q_\alpha q_\beta \cos\left[\mathbf{Q}.(\mathbf{R}+\mathbf{c}_\alpha-\mathbf{c}_\beta)\right]}{\mid \mathbf{R}+\mathbf{c}_\alpha-\mathbf{c}_\beta \mid} q_n\left[\frac{2 \mid \mathbf{R}+\mathbf{c}_\alpha-\mathbf{c}_\beta \mid}{R_0}-1\right] - \frac{q_\beta^2}{R_0}\delta_{n,0}$$

$$+\frac{1}{V(\Omega)}\sum_{\mathbf{G}}\sum_{\alpha} q_\alpha q_\beta \cos \mathbf{G}.(\mathbf{c}_\alpha-\mathbf{c}_\beta)\frac{4\pi}{\mid \mathbf{G}+\mathbf{Q} \mid^2}\cos\left[\frac{R_0}{2}\mid \mathbf{G}+\mathbf{Q} \mid\right] p_n\left[\frac{R_0}{2}\mid \mathbf{G}+\mathbf{Q} \mid\right]$$

in terms of the previously defined functions, $q_n(z)$ and $p_n(z)$.

There are two relatively simple cases; Firstly the case of a single atom per unit cell with a cunningly chosen phase:

$$I = \sum_{\mathbf{R}\neq\mathbf{0}} \frac{\cos\left[\mathbf{Q}.\mathbf{R}\right]}{\mid \mathbf{R} \mid} q_n\left[\frac{2 \mid \mathbf{R} \mid}{R_0}-1\right] - \frac{1}{R_0}\delta_{n,0}$$

$$+\frac{1}{V(\Omega)}\sum_{\mathbf{G}} \frac{4\pi}{\mid \mathbf{G}+\mathbf{Q} \mid^2}\cos\left[\frac{R_0}{2}\mid \mathbf{G}+\mathbf{Q} \mid\right] p_n\left[\frac{R_0}{2}\mid \mathbf{G}+\mathbf{Q} \mid\right]$$

and secondly the case without the cunningly chosen phase:

$$I_\beta = \sum_{\mathbf{R}\alpha}{}' \frac{q_\alpha q_\beta}{\mid \mathbf{R}+\mathbf{c}_\alpha-\mathbf{c}_\beta \mid} q_n\left[\frac{2 \mid \mathbf{R}+\mathbf{c}_\alpha-\mathbf{c}_\beta \mid}{R_0}-1\right] - \frac{q_\beta^2}{R_0}\delta_{n,0}$$

$$+\frac{1}{V(\Omega)}\sum_{\mathbf{G}}\sum_{\alpha} q_\alpha q_\beta \cos \mathbf{G}.(\mathbf{c}_\alpha-\mathbf{c}_\beta)\frac{4\pi}{\mid \mathbf{G} \mid^2}\cos\left[\frac{R_0}{2}\mid \mathbf{G} \mid\right] p_n\left[\frac{R_0}{2}\mid \mathbf{G} \mid\right]$$

You may like to consider the suitability of the functions:

$$q_m(z) = \int_z^1 \frac{du}{N_m}\exp\left(-\frac{1}{(1-u^2)^m}\right)$$

$$p_m(z) = \int_{-1}^1 \frac{du}{N_m}\cos zu \exp\left(-\frac{1}{(1-u^2)^m}\right)$$

in terms of the normalisation:

$$N_m = \int_{-1}^1 du \exp\left(-\frac{1}{(1-u^2)^m}\right)$$

as a *very* smooth splitting.