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The Finite Coulomb Lattice Sum

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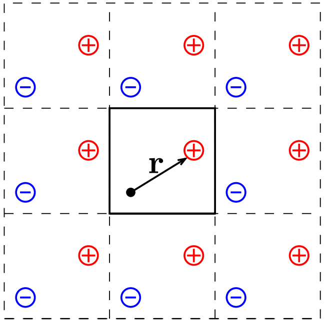
Coulomb Lattice Sum — The Madelung Problem



A two-particle unit cell:

Charges: $q = \pm 1$;

Lattice vectors:
$\mathbf{n} = (n_x, n_y, n_z) = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$
where $n_1, n_2, n_3 \in \mathcal{Z}$

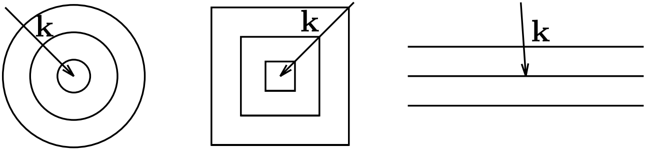
e.g. Cubic box of length L:
$\mathbf{n} = (n_1, n_2, n_3)L$

$$\nu(\mathbf{r}) = \frac{1}{|\mathbf{r}|} + \sum_{\mathbf{n}\neq\mathbf{0}}^{\infty}\left(\frac{1}{|\mathbf{r}+\mathbf{n}|} - \frac{1}{|\mathbf{n}|}\right); \quad \sum_{\mathbf{n}}^{\infty} = \sum_{n_1=-\infty}^{\infty}\sum_{n_2=-\infty}^{\infty}\sum_{n_3=-\infty}^{\infty}$$

Refs. Madelung (1918); Ewald (1921) Redlack and Grindlay (1972) Felderhof (1980) de Leeuw, Perram, and Smith (1980)(1981) etc.

Coulomb Lattice Sum — Infinite Boundary Term

$$\nu_{\mathrm{ib}}(\mathbf{r}) = -\frac{2\pi}{V} \lim_{\mathbf{k}|\mathbf{s}\to 0} \frac{(\mathbf{k}\cdot\mathbf{r})^2}{|\mathbf{k}|^2} = -\frac{2\pi}{V} \begin{cases} \dfrac{r^2}{3} = \dfrac{x^2+y^2+z^2}{3} \\ z^2 \end{cases}$$



spherical cubic xy-planar

Z. Hu "Infinite Boundary Terms of Ewald Sums and Pairwise Interactions for Electrostatics in Bulk and at Interfaces" *J. Chem. Theory Comput.* 10, 5254 (2014)

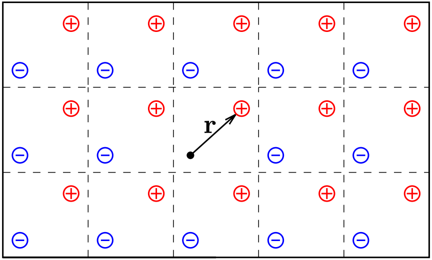
Coulomb Lattice Sum — Finite Crystals?

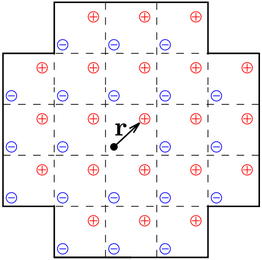
What is the boundary term of a finite Crystal?

Can we separate the boundary and finite-size effects for finite crystals?

Does the direct sum converge uniquely after removing boundary and finite-size effects?

Finite Lattice Sum — Exact Shape and Size





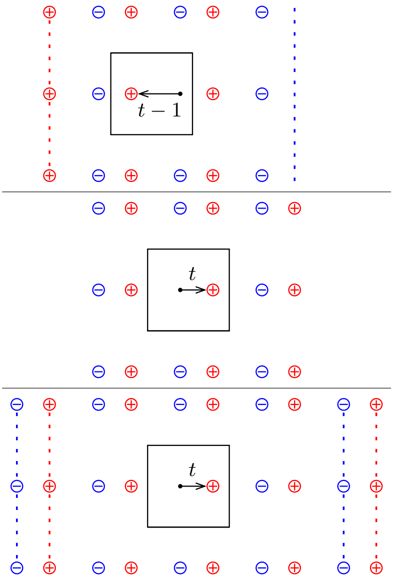
5×3

$3 \times 3 + 3 \times 1$
or
$5 \times 5 - 1 \times 1$

next-larger: 15×9

$9 \times 9 + 9 \times 3$
or
$15 \times 15 - 3 \times 3$

Finite Lattice Sum — Boundary Term



$\mathbf{r} = (t-1, 0, 0)$
$(2p+1) \times (2p+1) \times (2p+1)$

$\mathbf{r} = (t, 0, 0)$
$(2p+1) \times (2p+1) \times (2p+1)$

$\mathbf{r} = (t, 0, 0)$
$3(2p+1) \times (2p+1) \times (2p+1)$

Coulomb Lattice Sum — Finite Crystals

Define a Lattice of size p and shape $\mathbf{s} = (s_1, s_2, s_3)$: $L(p|\mathbf{s})$
$(2s_1+1)(2p+1) \times (2s_2+1)(2p+1) \times (2s_3+1)(2p+1)$

$$\nu(\mathbf{r}, p|\mathbf{s}) = \frac{1}{|\mathbf{r}|} + \sum_{\mathbf{n}\neq\mathbf{0}}^{L(p|\mathbf{s})} \left(\frac{1}{|\mathbf{r}+\mathbf{n}|} - \frac{1}{|\mathbf{n}|} \right)$$

$$\nu(\mathbf{r}, p|\mathbf{s}) = \nu_{\mathrm{pbc}}(\mathbf{r}) + \nu_{\mathrm{b}}(\mathbf{r}|\mathbf{s}) + \nu_{\mathrm{corr}}(\mathbf{r}, p|\mathbf{s})$$

$\nu_{\mathrm{pbc}}(\mathbf{r})$ — periodic, size-independent, shape-independent, bulk

$\nu_{\mathrm{b}}(\mathbf{r}|\mathbf{s})$ — boundary term, non-periodic, size-independent

$\nu_{\mathrm{corr}}(\mathbf{r}, p|\mathbf{s})$ — correction term, decaying to zero for $p \to \infty$

Zhao, He and Hu, "The Madelung Problem of Finite Crystals", *J. Chem. Theory Comput.* 22, 2790, (2026)

Finite Lattice Sum — Boundary/Correction Terms

$$\nu(\mathbf{r}, p|\mathbf{s}) = \frac{1}{|\mathbf{r}|} + \sum_{\mathbf{n}\neq\mathbf{0}}^{L(p|\mathbf{s})} \left(\frac{1}{|\mathbf{r}+\mathbf{n}|} - \frac{1}{|\mathbf{n}|} \right)$$

$$\nu(\mathbf{r}, p|\mathbf{s}) = \nu_{\mathrm{pbc}}(\mathbf{r}) + \nu_{\mathrm{b}}(\mathbf{r}|\mathbf{s}) + \nu_{\mathrm{corr}}(\mathbf{r}, p|\mathbf{s})$$

Dimensions of Crystals: a, b, c and $d = \sqrt{a^2 + b^2 + c^2}$:

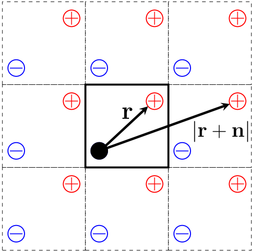
$$\nu_{\mathrm{b}}(\mathbf{r}|\mathbf{s}) = -\frac{4}{V}\left(x^2 \mathrm{atan}\frac{bc}{ad} + y^2 \mathrm{atan}\frac{ac}{bd} + z^2 \mathrm{atan}\frac{bc}{ad} \right)$$

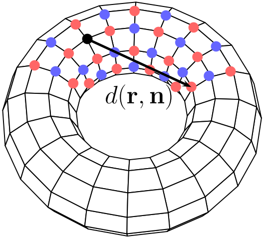
$V = L^3 = 1$:

$$\nu_{\mathrm{b}}(\mathbf{r}|\mathbf{s}) = -2\pi r^2/3,$$

$$\nu_{\mathrm{corr}}(\mathbf{r}, p|\mathbf{s}) = \frac{24r^4 - 40(x^4 + y^4 + z^4)}{9\sqrt{3}(2p+1)^2} + \mathcal{O}(p^{-4}).$$

Coulomb Lattice Sum — Clifford Supercell (CS)



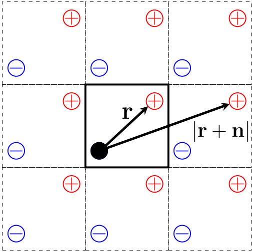


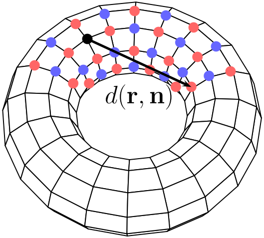
$$d(\mathbf{r},\mathbf{n}) = \frac{K}{\sqrt{2}\pi}\left[3 - \sum_{\alpha=1}^{3}\cos\frac{2\pi(\mathbf{r}+\mathbf{n})\cdot\mathbf{e}_\alpha}{K}\right]^{1/2},$$

$$\nu_{\mathrm{CS}}(\mathbf{r}) = \frac{1}{d(\mathbf{r},\mathbf{0})} + \sum_{\mathbf{n}\neq\mathbf{0}}\left[\frac{1}{d(\mathbf{r},\mathbf{n})} - \frac{1}{d(\mathbf{0},\mathbf{n})}\right].$$

Tavernier *et al. J. Phys. Chem. Lett.* 11, 7090 (2020); (2022), (2024) etc.

Madelung Constants — CsCl Crystal





CsCl Crystal: $\mathbf{r} = (0.5, 0.5, 0.5)$ Ref. 1.76 267 477 307

p	$\sqrt{3}\nu_{\rm pbc}(\mathbf{r})/2$	abs. error	$\sqrt{3}\nu_{\rm CS}(\mathbf{r})/2$	abs. error
1	1.7629780255	3.0×10^{-4}	1.408794	-3.5×10^{-1}
5	1.7626721815	-2.6×10^{-6}	1.744082	-1.9×10^{-2}
20	1.7626747599	-1.3×10^{-8}	1.761379	-1.3×10^{-3}
60	1.7626747729	-1.7×10^{-10}	1.762526	-1.5×10^{-4}

Zhao, He and Hu, "The Madelung Problem of Finite Crystals"
J. Chem. Theory Comput. 22, 2790, (2026)

Madelung Constants — Crystals

$NaCl$ (rocksalt), ZnS (zincblende), and CaF_2 (fluorite) with $p = 20$

method	NaCl	ZnS/Ca^{2+}	F^-
CS	1.7479628535	1.638065778	0.8811756598
EC	1.7475645804	1.638055048	0.8813373869
ref.	1.7475645946	1.638055053	0.8813373865

$CaTiO_3$:

ions	$p = 20$	ref.
Ca^{2+}	-2.693604868	-2.693604825
Ti^{4+}	-12.37746806	-12.37746803
O^{2-}	-3.227954396	-3.227954401
cell	-24.75493611	-24.75493606

Zhao, He and Hu, *J. Chem. Theory Comput.* 22, 2790, (2026)

Conditional Convergence — A Simple 1D Analogue

YES! $S = 1 - 1 + 1 - 1 + \cdots$

$S_- = (1-1)+(1-1)+\cdots = 0; \quad S_+ = 1+(-1+1)+(-1+1)+\cdots = 1$

S_{bulk} satisfies the periodicity, $S = 1 - S \Longrightarrow S = 1/2 = S_{\text{bulk}}$

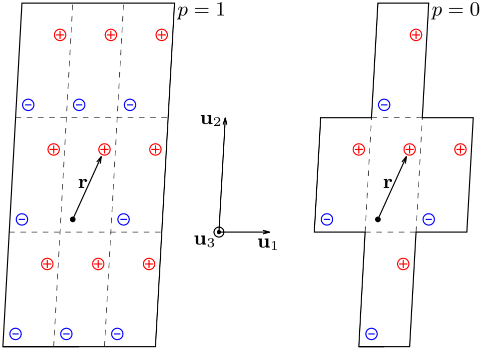
$$S_{\mp} = S_{\text{bulk}} \mp 1/2$$

$$\text{NO!} \quad 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots = \sum_{n=1}^{\infty} \left[\frac{1}{2n-1} - \frac{1}{2n} \right] = \ln 2$$

$$\left(1 - \frac{1}{2} - \frac{1}{4}\right) + \left(\frac{1}{3} - \frac{1}{6} - \frac{1}{8}\right) + \left(\frac{1}{5} - \frac{1}{10} - \frac{1}{12}\right) + \cdots = \frac{1}{2} \ln 2$$

Zhao and Hu "Infinite Boundary Terms and Pairwise Interactions: A Unified Framework for Periodic Coulomb Systems" *J. Chem. Theory Comput.* 21, 5916 (2025)

Arbitrary Shape in a Triclinic Lattice



He and Hu “The Finite Coulomb Lattice Sum: A Resolution of Conditional Convergence through Exact Shape and Size” *J. Phys. Chem. Letters* 17, 7501 (2026)
He and Hu “Analytic Boundary Terms for Arbitrary Crystal Geometries and Direct-Sum Evaluation of Madelung Constants in Triclinic Lattices” *J. Chem. Theory Comput.* 10.1021/acs.jctc.6c01289 (2026)

Conclusions

— The conditional convergence problem of Coulomb lattice sum can be resolved through exact shape and size.

— Direct summations with shape- and size-effect corrected yield extremely accurate Madelung constants without the need of the Ewald sum.

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