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Infinite Coulomb sums and Ewald summation

Consider the electrostatic energy of a set of point charges Q_j at $\vec{r}_j$:

$$E_H = \frac{1}{2} \sum_{i \neq j} \frac{Q_i Q_j}{\|\vec{r}_i - \vec{r}_j\|}$$

Due to the long range of $1/r$ this sum can be ill-defined for ∞ &/or periodic systems (IR divergence). So we first cut off the Coulomb $1/r$ potential at long distances $r > \Lambda$ & call it $v^\Lambda(r)$. Examples are

$$v^\Lambda(r) = \frac{e^{-r/\Lambda}}{r} \quad \text{Yukawa cutoff}$$

$$= \frac{\operatorname{erfc}(r/\Lambda)}{r} \quad \text{Gaussian (Ewald) cutoff}$$

We will later send $\Lambda \to +\infty$ & see what happens.

So

$$E_H^\Lambda = \frac{1}{2} \sum_{j \neq k} Q_j Q_k \, v^\Lambda(|\vec{r}_j - \vec{r}_k|)$$

Notice that $v^\Lambda(0)$ never occurs here so there is no short-ranged (UV) divergence possible.

To make some progress, we see that

$$E_H^\Lambda = \frac{1}{2} \sum_j Q_j \phi_j \,, \quad \phi_j = \sum_{k \neq j} Q_k \, v^\Lambda(|\vec{r}_k - \vec{r}_j|)$$

So the real challenge is to find ϕ_j.

<u>Elementary point</u>: even if ϕ_j is well-defined, the sum over j in $E_H^\Lambda = \frac{1}{2}\sum_j Q_j \phi_j$ may diverge simply because the number of charges is large or $\to \infty$. So we really should just focus on ϕ_j since it is intensive & $\phi_j/2$ is energy per particle per unit charge.

$$\phi_j = \sum_{k \neq j} Q_k v^\Lambda(r_{kj}) \quad : \quad \vec{r}_{kj} = \vec{r}_k - \vec{r}_j \ , \quad r_{kj} = \|\vec{r}_{kj}\|$$

This sum converges for $\Lambda > 0$ so we now find a good way to calculate it by splitting up v^Λ into a short-ranged & long-ranged part à-la-Ewald:

$$v^\Lambda(r) = \underbrace{v^\Lambda(r) - v^\lambda(r)}_{} + \underbrace{v^\lambda(r)}_{}$$

$$= \underset{\text{long-ranged}}{v_\ell(r)} + \underset{\text{short-ranged}}{v_s(r)}$$

where $\lambda \ll \Lambda$ is a microscopic cutoff used for efficient computation. λ is fixed.

$$\phi_j = \underbrace{\sum_{k \neq j} Q_k v_s(r_{kj})}_{\phi_{js}^\lambda} + \underbrace{\sum_{k \neq j} Q_k v_\ell(r_{kj})}_{\phi_{j\ell}^{\Lambda,\lambda}}$$

ϕ_{js}^λ is a rapidly convergent sum in real space & is not a worry

$$\phi_{j\ell} = \sum_k Q_k v_\ell(r_{kj}) - Q_j v_\ell(0)$$

where we added + subtracted j to unrestrict k-sum for Fourier analysis. We expect $v^\ell(0)$ to be finite as both v^Λ & v^λ behave as $1/r + O(r^0)$ as $r \to 0$ so the difference should be finite. Examples:

Yukawa case: $v_\ell(0) = \lim_{r\to 0} \frac{e^{-r/\Lambda} - e^{-r/\lambda}}{r} = \frac{1}{\lambda} - \frac{1}{\Lambda}$

Gaussian case: $v_\ell(0) = \lim_{r\to 0} \frac{\mathrm{erfc}(r/\Lambda) - \mathrm{erfc}(r/\lambda)}{r} = \frac{2}{\sqrt{\pi}}\left(\frac{1}{\lambda} - \frac{1}{\Lambda}\right)$

Also, the appearance of $v_\ell(0)$ is in some sense artificial since it is canceled by the $j=k$ term.

So $\phi_{j\ell} = \sum_k Q_k v_\ell(r_{kj}) - Q_j v_\ell(0)$, $v_\ell(0) \sim 1/\lambda - 1/\Lambda$

Now Fourier analyze $v_\ell(r) = \int \frac{d^3q}{(2\pi)^3} e^{i\vec{q}\cdot\vec{r}} \hat{v}_\ell(q)$

Examples: bare Coulomb $\frac{1}{r} \to 4\pi/q^2$

Yukawa $e^{-r/\Lambda}/r \to 4\pi/(q^2 + \Lambda^{-2})$

Gaussian $\frac{\mathrm{erfc}(r/\Lambda)}{r} \to \frac{4\pi}{q^2}\left(1 - e^{-q^2\Lambda^2/4}\right)$

$$\phi_{j\ell} = \int \frac{d^3q}{(2\pi)^3} \hat{v}_\ell(q) \sum_k Q_k e^{i\vec{q}\cdot\vec{r}_{kj}} - Q_j v_\ell(0)$$

$$= \int \frac{d^3q}{(2\pi)^3} \hat{v}_\ell(q) e^{-i\vec{q}\cdot\vec{r}_j} S(\vec{q}) - Q_j v_\ell(0)$$

$S(\vec{q}) \equiv \sum_k Q_k e^{i\vec{q}\cdot\vec{r}_k}$ is structure factor

The potentially troublesome part of the integral is around $\vec{q}=0$ where $\hat{v}_\ell(0)$ can become large as $\Lambda \to \infty$: e.g. $\hat{v}_\ell(q) = \frac{4\pi}{q^2+\Lambda^{-2}} - \frac{4\pi}{q^2+\lambda^{-2}}$

$$\hat{v}_\ell(0) = 4\pi(\Lambda^2-\lambda^2) \text{ for Yukawa}$$

$$\hat{v}_\ell(0) = \pi(\Lambda^2-\lambda^2) \text{ for Gaussian}$$

But for a neutral system, $\sum_k Q_k = S(0) = 0$ & $\hat{v}_\ell(0)$ is not relevant. If $S(0) \neq 0$, we <u>may</u> get in trouble.

To be more precise, we will assume a periodic system: lattice vectors $\vec{R}$ & positions in unit cell are $\vec{\tau}$. Then

$$S(\vec{q}) = \sum_k Q_k e^{i\vec{q}\cdot\vec{r}_k} = \sum_R \sum_\tau Q_\tau e^{i\vec{q}\cdot\vec{\tau}+i\vec{q}\cdot\vec{R}} = \sum_\tau Q_\tau e^{i\vec{q}\cdot\vec{\tau}} \underbrace{\sum_R e^{i\vec{q}\cdot\vec{R}}}_{\text{standard periodic sum}}$$

$$= \frac{(2\pi)^3}{\Omega}\sum_G \delta^{(3)}(\vec{q}-\vec{G})$$

Ω = volume of unit cell

$$S(\vec{q}) = \sum_\tau Q_\tau e^{i\vec{q}\cdot\vec{\tau}} \frac{(2\pi)^3}{\Omega}\sum_G \delta^{(3)}(\vec{q}-\vec{G})$$

So

$$\phi_{\tau\ell} = \sum_G e^{-i\vec{G}\cdot\vec{\tau}} \frac{\hat{v}_\ell(G)}{\Omega} s(G) - Q_\tau v_\ell(0)$$

$$s(G) = \sum_{\tau'} Q_{\tau'} e^{i\vec{G}\cdot\vec{\tau}'}$$

$$= \underbrace{\sum_{G\neq 0} e^{-i\vec{G}\cdot\vec{\tau}} \frac{\hat{v}_\ell(G)}{\Omega} s(G)}_{\text{rapidly convergent for large } \vec{G} \text{ since } \hat{v}_\ell(G)\to 0 \text{ faster than } 1/G^2 \text{ as } |\vec{G}|\to\infty} + \underbrace{\frac{\hat{v}_\ell(0)}{\Omega} s(0)}_{\text{troublesome if } S(0)\neq 0} - Q_\tau v_\ell(0)$$

For periodic system we then have

$$\phi_\tau = \sum_{R,\tau'} Q_{\tau'} v_s(\|\vec{R}+\vec{\tau}'-\vec{\tau}\|) + \sum_{G\neq 0} e^{-i\vec{G}\cdot\vec{\tau}} \frac{\hat{v}_\ell(G)}{\Omega} S(G) + \frac{\hat{v}_\ell(0) S(0)}{\Omega} - Q_\tau v_\ell(0)$$

- the first 2 terms converge very well.
- the third may be trouble
- the fourth is finite & λ dependent

$v_\ell(0) \sim 1/\lambda - 1/\Lambda$ is well-behaved for $\Lambda \to \infty$

$\hat{v}_\ell(0) \sim \Lambda^2 - \lambda^2$ is divergent for $\Lambda \to \infty$

So we need $S(0) = 0 = \sum_\tau Q_\tau$: net neutral unit cell

If $S(0) \neq 0$ answer is ∞ & certainly depends on details of cutoff for large but finite Λ.

When $\sum_\tau Q_\tau = 0$, we can send $\Lambda \to \infty$ & get a well-defined answer.

Final answer is:

$\longrightarrow$

① Let $S(G) = \sum_{\tau} Q_\tau e^{i\vec{G}\cdot\vec{\tau}}$; $S(0)=0$ required

② Pick finite λ & define

$$v_s(r) = v^\lambda(r)$$

$$v_\ell(r) = 1/r - v^\lambda(r) \qquad v_\ell(0) \sim 1/\lambda$$

③ Compute

$$\phi_\tau = \sum_{R,\tau'} Q_{\tau'} v^\lambda(\|\vec{R}+\vec{\tau}'-\vec{\tau}\|) + \sum_{G\neq 0} \frac{\hat{v}_\ell(G) e^{-i\vec{G}\cdot\vec{\tau}} S(\vec{G})}{\Omega}$$

$$- Q_\tau v_\ell(0)$$

④ $E_{\pi/cell} = \frac{1}{2} \sum_{\tau} Q_\tau \phi_\tau$