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Lattice sums for semiclassical Coulomb systems in periodic boundary conditions

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Abstract. Effective semiclassical potentials for the Coulomb interaction in two and three dimensions are calculated according to the prescription of Feynman and Hibbs. For these potentials, the Ewald transformation is obtained for the semiclassical Hamiltonian of a periodic array constructed from a unit cell containing a neutral assembly of charged particles.

In this note, we address the problem of deriving approximate Hamiltonians for the computer simulation of semiclassical Coulomb systems in two and three dimensions. To this end, we push aside the question of quantum dynamical effects, and focus on quantum corrections to equilibrium properties, using the path integral formulation of quantum statistical mechanics (Feynman and Hibbs 1964). The most useful result here is that if the interatomic potential between two particles is $\phi(x)$, then quantum effects may be approximated by calculating the classical partition function using the renormalised potential $V(x)$ given by

$$V(x) = (\lambda/\pi)^{1/2} \int_{-\infty}^{\infty} \Phi(x+y) \exp(-\lambda y^2)\, dy \tag{1}$$

where

$$\lambda = 6mk_B T/\hbar^2 \tag{2}$$

is the inverse square of the thermal wavelength. Equation (1), when expanded in powers of $\hbar^{-2}$, agrees to second order with the more usual Wigner–Kirkwood expansion. Most investigations of these renormalised potentials $V(x)$ have been for one-dimensional systems. We note that $V(x)$ defined by equation (1) only exists if $\phi(x)$ does not diverge faster than $|x|^{-1+\varepsilon}$, $\varepsilon > 0$ as $x \to 0$. The generalisation of equation (1) to higher dimensionality is straightforward. If $\phi(|\boldsymbol{r}|)$ is the classical potential, the renormalised $V(|\boldsymbol{r}|)$ in d-space is

$$V(|\boldsymbol{r}|) = (\lambda/\pi)^{d/2} \int_{R^d} \phi(|\boldsymbol{r}+\boldsymbol{y}|) \exp(-\lambda y^2)\, d\boldsymbol{y}. \tag{3}$$

In particular, $V(|\boldsymbol{r}|)$ exists for the Coulomb potentials

$$\Phi(|\boldsymbol{r}|) = q^2/|\boldsymbol{r}| \tag{4a}$$

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and

$$\Phi(|\boldsymbol{r}|) = -q^2 \log(|\boldsymbol{r}|) \tag{4b}$$

in three and two dimensions respectively.

For the purposes of computer simulation of systems acting through long-ranged potentials such as equation (4) it is necessary to calculate rapidly the potential energy U_N of N particles at positions $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N$ with charges $Z_1 q, Z_2 q, \ldots, Z_N q$ within a d-dimensional cube of side l, this cube being repeated regularly throughout space. That is, we require to calculate the lattice sum

$$U_N = \tfrac{1}{2} \sum_{\boldsymbol{n}}{}' \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} Z_\alpha Z_\beta V(|\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta + \boldsymbol{n}l|) \tag{5}$$

where the sum is over all d-dimensional lattice vectors $\boldsymbol{n}l$, the term $\boldsymbol{n} = \boldsymbol{0}$ being omitted if $\alpha = \beta$. Equation (5) exists as a conditionally convergent series if the system is neutral, i.e. if

$$\sum_{\alpha} Z_\alpha = 0. \tag{6}$$

We return to the computation of equation (5) after we have computed equation (3) for the potentials (4a, b). We begin with the three-dimensional case (4a). We have, setting $|\boldsymbol{r}| = r$, $|\boldsymbol{y}| = y$, etc,

$$\begin{aligned} V(r) &= (\lambda/\pi)^{3/2} q^2 \int |\boldsymbol{r} + \boldsymbol{y}|^{-1} \exp(-\lambda y^2)\, \mathrm{d}\boldsymbol{y} \\ &= (\lambda/\pi)^{3/2} q^2 \int |\boldsymbol{s}|^{-1} \exp[-\lambda(r^2 - 2\boldsymbol{s}\cdot\boldsymbol{r} + s^2)]\, \mathrm{d}\boldsymbol{s}. \end{aligned} \tag{7}$$

To perform the integral over $\boldsymbol{s}$ we transform to a set of polar coordinates with the s_z axis parallel to $\boldsymbol{r}$. Then after some straightforward manipulations, we find

$$V(|\boldsymbol{r}|) = q^2 \operatorname{erf}(|\boldsymbol{r}|\sqrt{\lambda})/|\boldsymbol{r}| \tag{8}$$

where $\operatorname{erf}(x)$ is the usual error function (Abramowitz and Stegun 1964), defined by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-u^2)\, \mathrm{d}u. \tag{9}$$

Equation (8) has a couple of interesting properties. Firstly, $V(|\boldsymbol{r}|)$ is finite as $|\boldsymbol{r}| \to 0$, tending to the value $2q^2(\lambda/\pi)^{1/2}$. Secondly, we recover the classical potential (4a) as $\lambda \to \infty$ (either $T \to \infty$ or $\hbar \to 0$ according to taste), but for large values of λ, equation (8) possesses only an asymptotic expansion. Thirdly, a slight change of variable in equations (8) and (9) enables us to write $V(|\boldsymbol{r}|)$ as

$$V(|\boldsymbol{r}|) = \frac{q^2}{\sqrt{\pi}} \int_0^\lambda t^{-1/2} \exp(-tr^2)\, \mathrm{d}t \tag{10}$$

to which form we return after studying the two-dimensional case (4b). For this

$$V(|\boldsymbol{r}|) = -q^2(\lambda/\pi) \int \log(|\boldsymbol{s}|) \exp[-\lambda(s^2 - 2\boldsymbol{s}\cdot\boldsymbol{r} + r^2)]\, \mathrm{d}\boldsymbol{s} \tag{11}$$

which, after changing to polar coordinates with the s_x axis lying parallel to $\boldsymbol{r}$, becomes

$$V(|\boldsymbol{r}|) = -q^2(\lambda/\pi)\int_0^\infty s\,\mathrm{d}s\log(s)\exp[-\lambda(s^2+r^2)]\int_0^{2\pi}\exp(2\lambda sr\cos\theta)\,\mathrm{d}\theta$$

$$= -2\lambda q^2\exp(-\lambda r^2)\int_0^\infty s\,\mathrm{d}s\log(s)\exp(-\lambda s^2)I_0(2\lambda sr) \tag{12}$$

where $I_0(z)$ is the modified Bessel function. This integral, or any simple transformed form of it, does not seem to be tabulated. To reduce it to a standard function, we set $u = s^2$ and write $V(|\boldsymbol{r}|)$ as

$$V(|\boldsymbol{r}|) = -\tfrac{1}{2}\lambda q^2\exp(-\lambda r^2)\int_0^\infty \log(u)\,\mathrm{d}u\exp(-\lambda u)I_0(2\lambda r\sqrt{u}). \tag{13}$$

As the series expansion

$$I_0(2\lambda r\sqrt{u}) = \sum_{n=0}^{\infty}(\lambda r)^{2n}u^n/(n!)^2 \tag{14}$$

is uniformly and absolutely convergent for any u, we may substitute (14) into (13) and integrate term by term, using the standard Laplace transform (Erdelyi *et al* 1954)

$$\int_0^\infty u^n\log(u)\,\mathrm{e}^{-\lambda u}\,\mathrm{d}u = -\lambda^{-1}(\log\lambda+\gamma), \qquad n=0, \tag{15a}$$

$$= \lambda^{-n-1}n!\Big(\sum_{k=1}^{n}k^{-1}-\log\lambda-\gamma\Big), \qquad n=1,2,\ldots, \tag{15b}$$

where γ is the Euler constant. We now write

$$\sum_{k=1}^{n}k^{-1} = \int_0^1\sum_{k=1}^{n}t^{k-1}\,\mathrm{d}t = \int_0^1\frac{1-(1-t)^n}{t}\,\mathrm{d}t \tag{16}$$

noting that if we agree to define $\Sigma_{k=1}^{n}k^{-1}$ to be zero for $n=0$, equation (16) also holds for $n=0$ and equation (15a) becomes superfluous. Then

$$V(|\boldsymbol{r}|) = -\tfrac{1}{2}q^2\exp(-\lambda r^2)\sum_{n=0}^{\infty}\frac{(\lambda r^2)^n}{n!}\Big(\int_0^1\frac{1-(1-t)^n}{t}\,\mathrm{d}t-\log\lambda-\gamma\Big). \tag{17}$$

We now interchange the orders of summation and integration to obtain

$$V(|\boldsymbol{r}|) = -\tfrac{1}{2}q^2\Big(\int_0^1\frac{1-\exp(-\lambda r^2t)}{t}\,\mathrm{d}t-\log\lambda-\gamma\Big). \tag{18}$$

This step may be justified by either expanding equations (13) and (18) in powers of (λr^2) and comparing coefficients or by inserting ε for zero in the lower limit of equation (16) and using the principle of analytic continuation. It now remains to set $u = \lambda r^2 t$ in equation (18) and recognise that

$$\int_0^x t^{-1}(1-\mathrm{e}^{-t})\,\mathrm{d}t = E_1(x)+\log x+\gamma$$

where $E_1(x)$ is the exponential integral function (Abramowitz and Stegun 1964). We thus find for $V(|\boldsymbol{r}|)$ the form

$$V(|\boldsymbol{r}|) = -\tfrac{1}{2}q^2[\log(|\boldsymbol{r}|^2)+E_1(\lambda|\boldsymbol{r}|^2)]. \tag{19}$$

We note that, in passing, we have derived the Laplace transform

$$\int_0^\infty \mathrm{d}u \log u \, \mathrm{e}^{-pu} I_0(\mu\sqrt{u}) = p^{-1} \exp(\mu^2/4p)[\log(\mu^2/4p) + E_1(\mu^2/4p)]. \tag{20}$$

To see that equation (19) tends to a finite value as $|\boldsymbol{r}| \to 0$, we use the expansion

$$E_1(z) = -\gamma - \log z + \mathrm{O}(z)$$

to find

$$\lim_{r\to 0} V(r) = \tfrac{1}{2}q^2(\gamma + \log\lambda). \tag{21}$$

To put equation (19) in a form suitable for carrying out the lattice sum (5), we use the identity (Perram and de Leeuw 1981)

$$-\sum_{\alpha=1}^{N} z_\alpha \log(\boldsymbol{r}_\alpha^2) = \int_0^\infty t^{-1}\,\mathrm{d}t \sum_{\alpha=1}^{N} z_\alpha \exp(-\boldsymbol{r}_\alpha^2 t)$$

and rewrite the exponential integral in equation (19) as

$$E_1(\lambda r^2) = \int_\lambda^\infty t^{-1}\,\mathrm{d}t \exp(-r^2 t).$$

We further note that the charges at $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$ interact with themselves with an energy

$$U_{\mathrm{SELF}} = \tfrac{1}{2}q^2\left(\sum_{\alpha=1}^{N} z_\alpha^2\right)(\gamma + \log\lambda)$$

which is finite and may thus be included in the lattice sum (5). We thus have

$$\begin{aligned} U_N &= \tfrac{1}{2}U_{\mathrm{SELF}} + \tfrac{1}{2}\sum_{\boldsymbol{n}}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta V(|\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta + \boldsymbol{n}l|) \\ &= \tfrac{1}{4}q^2\left(\sum_{\alpha=1} z_\alpha^2\right)(\gamma + \log\lambda) + \tfrac{1}{4}q^2\sum_{\boldsymbol{n}}\int_0^\lambda \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta t^{-1}\exp[-t(r_\alpha - r_\beta + nl)^2]\,\mathrm{d}t \end{aligned} \tag{22}$$

where the sum is now over all lattice vectors $\boldsymbol{n}$. A similar lattice sum may be written for three-dimensional charges. We see that here

$$U_{\mathrm{SELF}} = 2q^2(\lambda/\pi)^{1/2}\left(\sum_{\alpha=1}^{N} z_\alpha^2\right)$$

so that, including self-energy terms,

$$U_N = q^2(\lambda/\pi)^{1/2}\left(\sum_{\alpha=1}^{N} z_\alpha^2\right) + \tfrac{1}{2}q^2\pi^{-1/2}\sum_{\boldsymbol{n}}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \int_0^\lambda t^{-1/2}\,\mathrm{d}t \exp[-t(\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta + \boldsymbol{n}l)^2]. \tag{23}$$

Equations (22) and (23) are strikingly similar to the corresponding forms for classical lattice sums, the only difference being that the term $\boldsymbol{n} = \boldsymbol{0}$ is included (which makes the calculation easier) and that the upper limits on the integrals are λ instead of infinity.

We now sketch the conversion of equations (22) and (23) into rapidly computable forms. We define $U_N(s)$ by replacing $\Sigma_{\boldsymbol{n}}$ by $\Sigma_{\boldsymbol{n}} \exp(-s\boldsymbol{n}^2)$ in both cases, and also define

$$u = tl^2, \qquad \boldsymbol{R}_\alpha = \boldsymbol{r}_\alpha / l.$$

Equations (22) and (23) then become

$$U_N(s) = \tfrac{1}{4}q^2\Big(\sum_{\alpha=1}^{N} z_\alpha^2\Big)(\gamma + \log\lambda) + \tfrac{1}{4}q^2 \sum_{\boldsymbol{n}} \int_0^{\lambda l^2} \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \exp[-u\boldsymbol{R}_{\alpha\beta}^2 - 2u\boldsymbol{n}\cdot\boldsymbol{R}_{\alpha\beta} - (u+s)\boldsymbol{n}^2]u^{-1}\,\mathrm{d}u \tag{24}$$

in two dimensions, and

$$U_N(s) = q^2(\lambda/\pi)^{1/2}\Big(\sum_{\alpha=1}^{N} z_\alpha^2\Big) + \tfrac{1}{2}q^2 l^{-1}\pi^{-1/2}\sum_{\boldsymbol{n}}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\int_0^{\lambda l^2} z_\alpha z_\beta \exp[-u\boldsymbol{R}_{\alpha\beta}^2 - 2u\boldsymbol{n}\cdot\boldsymbol{R}_{\alpha\beta} - (u+s)\boldsymbol{n}^2]u^{-1/2}\,\mathrm{d}u \tag{25}$$

in three.

The series in equations (24) and (25) are now absolutely and uniformly convergent for $\mathrm{Re}(s) > 0$. We now use the identity

$$(u+s)\boldsymbol{n}^2 + 2u\boldsymbol{n}\cdot\boldsymbol{R} = (u+s)\Big(\boldsymbol{n} + \frac{u}{u+s}\boldsymbol{R}\Big)^2 - \frac{u^2}{u+s}\boldsymbol{R}^2 \tag{26}$$

and the d-dimensional form of the Poisson summation formula applied to the gaussian function, namely

$$\sum_{\boldsymbol{n}} \exp[-\nu(\boldsymbol{n}+\boldsymbol{s})^2] = \sum_{\boldsymbol{n}} \Big(\frac{\pi}{\nu}\Big)^{d/2} \exp(-\pi^2\boldsymbol{n}^2/\nu + 2\pi i\boldsymbol{n}\cdot\boldsymbol{s}) \tag{27}$$

which for small $|\nu|$ converts a slowly convergent series into a rapidly convergent one. The sum over $\boldsymbol{n}$ may then be taken through the integral sign in equations (24) and (25), and, depending on the value of λl^2 (a point we return to in a moment), the integral splits into one from 0 to a parameter ν^2 plus one from ν^2 to λl^2. The optimal value of ν^2 is about π, since both series in equation (27) are approximately equally rapidly convergent for $\nu = \pi$. Of course, if $\lambda l^2 < \pi$, no such splitting is necessary. Assuming $\lambda^2 > \pi$, the integrals from ν to λl^2 may be expressed without further ado as rapidly convergent series of exponential integrals and error functions respectively. The transformation (27) is applied to the integrals from 0 to ν^2. The relevant parts of equations (24) and (25) are after transformation

$$U_N^I(s) = \frac{\pi q^2}{4}\int_0^{\nu^2} \frac{\mathrm{d}u}{u(u+s)} \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{\boldsymbol{n}} z_\alpha z_\beta \times \exp[-usR_{\alpha\beta}^2/(u+s) - \pi^2\boldsymbol{n}^2/(u+s) + 2\pi i u\boldsymbol{n}\cdot\boldsymbol{R}_{\alpha\beta}/(u+s)] \tag{28}$$

and, in three dimensions,

$$U_N^I(s) = \frac{\pi q^2}{2l}\int_0^{\nu^2} \frac{\mathrm{d}u}{u^{1/2}(u+s)^{3/2}} \sum_{\alpha=1}^{N}\sum_{\beta=1}^{N}\sum_{\boldsymbol{n}} z_\alpha z_\beta \times \exp[-usR_{\alpha\beta}^2/(u+s) - \pi^2\boldsymbol{n}^2/(u+s) + 2\pi i u\boldsymbol{n}\cdot\boldsymbol{R}_{\alpha\beta}/(u+s)]. \tag{29}$$

For $\boldsymbol{n}=0$, the integrals in equations (28) and (29) are divergent as $s\to 0$. This divergence is a consequence of the long-range nature of the Coulomb interactions. By making an asymptotic expansion in powers of s it is straightforward to show that the divergent terms vanish because of charge neutrality. The $\boldsymbol{n}=0$ term in equation (28) is

$$\frac{\pi q^2}{4}\int_0^{\nu^2}\frac{\mathrm{d}u}{u(u+s)}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \exp[-us\boldsymbol{R}_{\alpha\beta}^2/(u+s)]$$
$$=\frac{\pi q^2}{4}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \sum_{k=0}^{\infty}\frac{(-1)^k}{k!}s^k \boldsymbol{R}_{\alpha\beta}^{2k}\int_0^{\nu^2}\mathrm{d}u\frac{u^{k-1}}{(u+s)^{k+1}}. \tag{30}$$

We now note that, for $k\geqslant 1$,

$$\int_0^{\nu^2}\mathrm{d}u\frac{u^{k-1}}{(u+s)^{k+1}}\leqslant\int_0^{\nu^2}\frac{\mathrm{d}u}{(u+s)^2}=\frac{\nu^2}{s(\nu^2+s)}, \tag{31}$$

the equality holding for $k=1$. For $k=0$ we have

$$\frac{\pi q^2}{4}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta\int_0^{\nu^2}\frac{\mathrm{d}u}{u+s}=0 \tag{32}$$

because of the charge neutrality condition equation (6). Thus the $\boldsymbol{n}=0$ term in equation (28) becomes

$$\frac{\pi q^2}{4}\int_0^{\nu^2}\frac{\mathrm{d}u}{u(u+s)}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \exp\left(\frac{-us\boldsymbol{R}_{\alpha\beta}^2}{(u+s)}\right)$$
$$=\frac{\pi q^2}{4}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \boldsymbol{R}_{\alpha\beta}^2+\mathrm{O}(s)=\frac{\pi q^2}{2}\left(\sum_{\alpha=1} z_\alpha \boldsymbol{R}_\alpha\right)^2+\mathrm{O}(s)$$

where in the last step we have used the charge neutrality condition again. We may now take the limit $s\to 0$. Equation (28) then becomes

$$U_n^I(0)=\frac{\pi q^2}{2}\left(\sum_{\alpha=1}^{N} z_\alpha R_\alpha\right)^2+\frac{q^2}{4\pi}\sum_{\boldsymbol{n}\neq 0}\frac{\exp(-\pi^2 n^2/\nu^2)}{\boldsymbol{n}^2}\left|\sum_{\alpha=1}^{N} z_\alpha \exp(2\pi i\boldsymbol{n}\cdot\boldsymbol{R}_\alpha)\right|^2. \tag{33}$$

Similarly the $\boldsymbol{n}=\boldsymbol{0}$ term in equation (29) yields

$$\frac{\pi q^2}{2l}\int_0^{\nu^2}\frac{\mathrm{d}u}{u^{1/2}(u+s)^{3/2}}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \exp\left(\frac{-us\boldsymbol{R}_{\alpha\beta}^2}{(u+s)}\right)$$
$$=\frac{-\pi q^2}{3l}\frac{\nu^3}{(\nu^2+s)^{3/2}}\sum_{\alpha=1}^{N}\sum_{\beta=1}^{N} z_\alpha z_\beta \boldsymbol{R}_{\alpha\beta}^2+\mathrm{O}(s) \tag{34}$$

so that equation (29) gives

$$U_N^I(0)=\left(\frac{2\pi q^2}{3l}\right)\left(\sum_{\alpha=1} z_\alpha \boldsymbol{R}_\alpha\right)^2+\frac{q^2}{\pi}\sum_{\boldsymbol{n}\neq 0}\frac{\exp(-\pi^2\boldsymbol{n}^2/\nu^2)}{n^2}\left|\sum_{\alpha=1}^{N} z_\alpha \exp(2\pi i\boldsymbol{n}\cdot\boldsymbol{R}_\alpha)\right|^2. \tag{35}$$

For sufficiently low temperatures, it is possible that $\lambda l^2\leqslant\pi$. In this event

$$U_N(0)=U_N^I(0)$$

with ν^2 in equations (30) and (31) being replaced by λl^2. This has practical implications for the computer simulation of the system. This is because the only places where the

coordinates occur in equations (33) and (35) are in the terms

$$\sum_{\alpha=1}^{N} z_\alpha \exp(2\pi i \boldsymbol{n} \cdot \boldsymbol{R}_\alpha)$$

which means that the effective Hamiltonian may be expressed as one-particle sums.

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