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Note

Fourier Representation of the Coulombic Contributions to Polymer Chains

I. INTRODUCTION

Slowly convergent lattice summations arise in quantum-mechanical studies of chainlike systems. One possible approach to calculate them is by using the Fourier representation expressions for classical linear arrays of charges. Applicability of these formulas is considered and a substitute is derived for those cases where already existing formulas are no longer optimal.

The Hartree–Fock–Roothaan (LCAO–SCF–CO) method is now widely applied to calculate the electronic structure of infinite chainlike systems [1–3]. This method is used mainly to interpret and predict physico-chemical properties of polymers and other quasi-one-dimensional systems such as the interpretation of polymer XPS spectra, estimation of carrier mobilities, and studies of the electron distribution during the process of chemical bonding. Calculation of the total energy in these quasi-one-dimensional systems is difficult, due to convergence problems with respect to the number of interacting neighbors. Detailed numerical experimentations have been devoted to this question [4–6] and, only recently, a satisfactory solution was proposed [7]. The essence of this approach is to recognize that beyond a certain distance of interactions and, for a not too delocalized atomic basis set, the contributions to the Fock matrix elements and the total energy are of purely electrostatic nature. Exact expressions simplify into classical, point-charge interactions, and the associated numerical effort is at the same level of difficulty as that encountered in classical Madelung summations. The problem reduces finding an efficient procedure for evaluating lattice sums over one-dimensional arrays assuming, as required by the theoretical model, it extends to infinity. Due to the relatively large number of such lattice sums that have been performed in actual calculations, fast and accurate techniques are preferred. So far, in the context of the LCAO–SCF–CO procedure, two approaches have been considered: The first one is based on a two-center expansion of the Coulomb operator [8], and the second [9] applies the Fourier representation method, originally developed by Harris and co-workers [10–12].

In this paper, we comment on the actual applicability of Fourier representation formulas to the problems mentioned above, and we propose replacing the original expressions by more efficient ones in the ranges where the former are no longer optimal.

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II. Fourier Representation Expressions

In the framework of the Fourier representation method, a general expression for evaluating Madelung sums, $\mathscr{V}(\mathbf{s}_n)$

$$\mathscr{V}(\mathbf{s}_n) = \sum_{h=-\infty}^{+\infty} \sum_{m=1}^{d}{}' \frac{Q_m}{|\, ha\hat{z} + \mathbf{s}_m - \mathbf{s}_n \,|} \tag{1}$$

has been obtained [12]:

$$\mathscr{V}(\mathbf{s}_n) = -\frac{4}{a} Q_m \ln 2 + \frac{4}{a} \sum_{m=1}^{d}{}' Q_m \times \left(\sum_{\mu=1} \cos\left(\frac{2\pi}{a} \mu s_z^{mn}\right) K_0\left(\frac{2\pi}{a} \mu s_2^{mn}\right) - \frac{1}{2} \ln\left(\frac{2s_2^{mn}}{a}\right) - \frac{\gamma}{2} \right). \tag{2}$$

We are concerned with periodic lattices in which cells are electrically neutral ($Q_1 + Q_2 + \cdots + Q_d \equiv 0$). $\mathbf{s}_m$ denotes the location of charges Q_m in each cell and $\mathbf{s}^{mn}$ is the vector defined by $\mathbf{s}_m - \mathbf{s}_n$. The quantities s_z^{mn} and s_2^{mn} represent $|\, s_z^m - s_z^n \,|$ and $[(s_x^m - s_x^n)^2 + (s_y^m - s_y^n)^2]^{1/2}$ and a is the unit cell length. Figure 1 illustrates geometrically the quantities. The prime on the summation symbol indicates that $Q_m = Q_n$ has to be excluded; γ (= 0.5772156649) is the Euler constant.

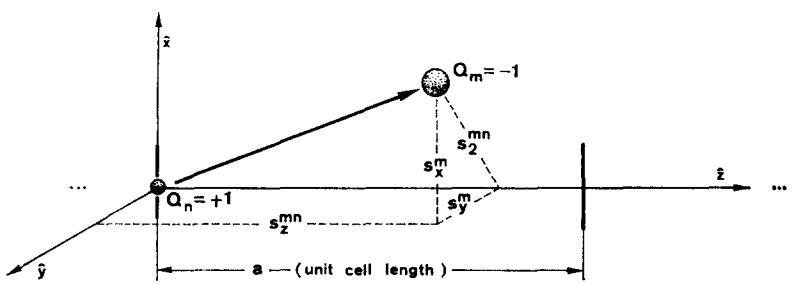

FIG. 1. Location of two point charges, $Q_n = +1$ and $Q_m = -1$, in the unit cell.

Equation (2) is of general applicability except when $s_2^{mn} \equiv 0$, which means that Q_m and Q_n lie on the same line parallel to the axis of periodicity, $\hat{z}$. In this event the Q_m contribution can be computed according to [9]

$$Q_m - \text{contribution} = -\frac{Q_m}{a}\left[2\Psi\left(\frac{s_z^{mn}}{a}\right) + \cot\left(\frac{\pi s_z^{mn}}{a}\right) + 2(\gamma + 2\ln 2)\right]. \tag{3}$$

$\Psi(x)$ is the digamma function, which is efficiently evaluated by using an expansion in Chebyshev polynomials [13].

As indicated in the original paper [12], Eq. (2) still contains an infinite summation;

however, the Bessel function, $K_0(x)$, causes the sum to be exponentially convergent. This is evident from the fact that for large values of the argument x, $K_0(x)$, can be approximated by (see [14, Eq. 9.7.2])

$$K_0(x) \simeq \left(\frac{\pi}{2x}\right)^{1/2} e^{-x}\left[1 - \frac{1}{8x} + \frac{9}{2(8x)^2}\right]. \tag{4}$$

In actual polymer calculations, however, x is related to differences between centers of charges and might become small, though not identically zero. In such cases, the exponential behavior disappears and Eq. (4) is no longer appropriate. The right limiting form is now (see [14, Eq. 9.6.8])

$$K_0(x) \sim -\ln(x). \tag{5}$$

Such series involving logarithms are known for their poor convergence; and, consequently, whenever s_2^{mn} is small enough so that

$$\sum_{\mu=1}^{\infty} \cos\left(\frac{2\pi}{a}\,\mu s_z^{mn}\right) K_0\left(\frac{2\pi}{a}\,\mu s_2^{mn}\right) \tag{6}$$

is hard to evaluate, another expression should be used. The way Eq. (6) behaves for small s_2^{mn}'s is illustrated in Table I, where values corresponding to the test case pictured in Fig. 1 are collected. When s_2^{mn} is smaller than 0.1, it is appropriate to use a more efficient way of evaluating Eq. (6), since it frequently occurs in actual problems.

III. Expression for Small s_2^{mn}'s

The practical difficulties associated with small values of s_2^{mn} in the evaluation of Eq. (6) can be overcome by using the following integral representation of $K_0(nb)$ (see [14, Eq. 11.4.44]):

$$K_0(nb) = \int_0^{\infty} \frac{xJ_0(bx)\,dx}{n^2 + x^2} \qquad (n > 0, b > 0) \tag{7}$$

together with (see [15, Eq. III–3c.b. 1])

$$\sum_{n=1}^{\infty} \frac{\cos(nc)}{n^2 + x^2} = -\frac{1}{2x^2} + \frac{\pi \cosh[x(\pi - c)]}{2x \sinh(\pi x)}. \tag{8}$$

For simplification, we have defined $b = (2\pi/a)\, s_2^{mn}$ and $c = (2\pi/a)\, s_z^{mn}$. After insertion of Eqs. (7) and (8) into Eq. (6) the latter now reads

$$\sum_{n=1}^{\infty} \cos(nc)\, K_0(nb) = \int_0^{\infty} xJ_0(bx)\left\{-\frac{1}{2x^2} + \frac{\pi \cosh[x(\pi - c)]}{2x \sinh(\pi x)}\right\} dx. \tag{9}$$

TABLE I

Values of $S(M, s_x^{mn}, s_z^{mn}) = \sum_{\mu=1}^{M} \cos((2\pi/a)\,\mu\, s_z^{mn})\, K_0((2\pi/a)\,\mu\, s_x^{mn})$.

M \ s_{xy}^{mn}	$s_z^{mn} = 0.1$				$s_z^{mn} = 0.3$			
	1.0	0.1	0.01	0.001	1.0	0.1	0.01	0.001
10	−0.23483066779	−7.0814738354	−10.697913126	−14.799155486	−0.23072612488	−3.3791809332	−4.9328894505	−9.1910857295
10^2	−0.23483066779	−7.0827490809	−9.9756870689	−11.426874418	−0.23072612488	−3.3782102754	−3.5678138383	−5.0399034632
10^3	−0.23483066779	−7.0827490809	−9.9744958903	−10.025517566	−0.23072612488	−3.3782102754	−3.5660753233	−3.5699197132
10^4	−0.23483066779	−7.0827490809	−9.9744958903	−10.023749332	−0.23072612488	−3.3782102754	−3.5660753233	−3.5680960194
2×10^4	−0.23483066779	−7.0827490809	−9.9744958903	−10.023749332	−0.23072612488	−3.3782102754	−3.5660753233	−3.5680960194

The interchange of the order of the summation and integration is legitimate, since the uniform convergence of the series is satisfied everywhere under the conditions $n > 0$ and $b > 0$. After elementary manipulations, we end up with

$$\sum_{n=1}^{\infty} \cos(nc)\, K_0(nb) = \frac{1}{2}\int_0^{\infty} dx\, J_0(bx)\left\{-\frac{1}{x} + \frac{\pi[e^{-cx} + e^{-(2\pi-c)x}]}{(1 - e^{-2\pi x})}\right\}. \tag{10}$$

We now divide the integration into regions, each of which will be suitable for efficient evaluation. Assuming that we aim for six significant figures and due to the fact that for $x \geqslant 3.0$, $\exp(-2\pi x)$ is less than 10^{-8}, Eq. (10) can be broken into two parts

$$\sum_{n=1}^{\infty} \cos(nc)\, K_0(nb) \simeq -\frac{1}{2}\int_0^3 \frac{dx}{x} J_0(bx)\left\{1 - \frac{\pi x[e^{-cx} + e^{-(2\pi-c)x}]}{(1 - e^{-2\pi x})}\right\}$$
$$-\frac{1}{2}\int_3^{\infty} \frac{dx}{x} J_0(bx)\{1 - x\pi[e^{-cx} + e^{-(2\pi-c)x}]\}. \tag{11}$$

This can be rearranged to

$$\sum_{n=1}^{\infty} \cos(nc)\, K_0(nb) \simeq \frac{1}{2}\int_0^3 dx\, J_0(bx)\left\{-\frac{1}{x} + \frac{\pi[e^{-cx} + e^{-(2\pi-c)x}]}{e^{2\pi x} - 1}\right\}$$
$$-\frac{1}{2}\int_3^{\infty} \frac{dx}{x} J_0(bx) + \frac{\pi}{2}\int_0^{\infty} [e^{-cx} + e^{-(2\pi-c)x}]\, J_0(bx)\, dx. \tag{12}$$

Using the result (see [16], Eq. 6.611–1),

$$\int_0^{\infty} e^{-cx} J_0(bx)\, dx = (c^2 + b^2)^{-1/2}, \tag{13}$$

we finally obtain

$$\sum_{n=1}^{\infty} \cos(nc)\, K_0(nb) \simeq \frac{1}{2}\int_0^3 dx\, J_0(bx)\left\{-\frac{1}{x} + \pi\left[\frac{e^{-cx} + e^{-(2\pi-c)x}}{e^{2\pi x} - 1}\right]\right\}$$
$$-\frac{1}{2} J_{i0}(3b) + \frac{\pi}{2}\left\{\frac{1}{[b^2 + c^2]^{1/2}} + \frac{1}{[b^2 + (2\pi - c)^2]^{1/2}}\right\}. \tag{14}$$

We were unable to find an appropriate tabular entry for the integral in the right-hand side of Eq. (14), but it is easily handled by numerical integration. Figure 2 shows the graph of the integrand for various values of s_z^{mn} in the case of $s_2^{mn} = 10^{-1}$. It is a well-behaved function. For very small x, a series expansion is recommended to avoid numerical inaccuracies due to cancellation of large values

$$-\frac{1}{x} + \pi\left[\frac{e^{-cx} + e^{-(2\pi-c)x}}{e^{2\pi x} - 1}\right] \simeq \delta + \pi\epsilon(1 + x\delta) - \pi[\sinh(cx) + e^{-cx} + e^{-(2\pi-c)x}]. \tag{15}$$

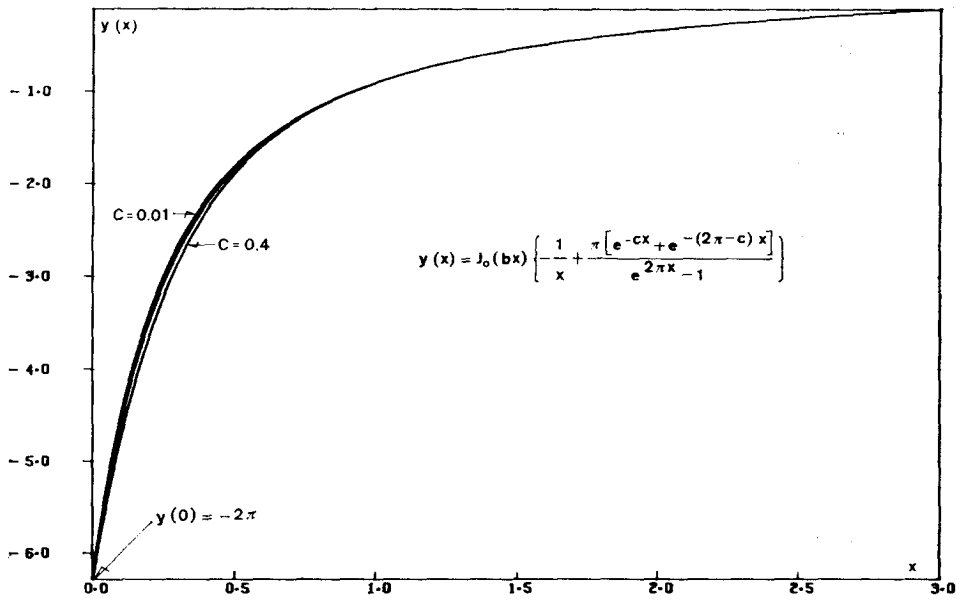

FIG. 2. Graph of $y(x) = J_0(bx)\{-1/x + \pi\,[e^{-cx} + e^{-(2\pi-c)x}\}]/(e^{2\pi x} - 1)$ for three values of c (from left to right curve $c/2\pi = 0.01$, 0.1, and 0.4). The values of b and a are 0.2π and 1.0π, respectively.

with

$$\delta = \frac{c^2x}{2} + \frac{c^4x^3}{24} + \frac{c^6x^5}{720} + \cdots \qquad \text{and} \qquad \epsilon = \frac{\pi x}{3} - \frac{(\pi x)^3}{45} + 2\,\frac{(\pi x)^5}{945}. \quad (16)$$

The presence of the Bessel function $J_0(bx)$ as a factor in the integrand affects the shape of the graph very little, since actual values of b $(= (2\pi/a)\, s_2^{mn})$ are small enough to confine bx close to the origin when x varies from 0.0 to 3.0. Equation (14) is, therefore, well suited for those cases $(s_2^{mn} \leqslant 0.1)$ where direct summation in Eq. (6) becomes prohibitive. Equation (14) is not adapted for large values of b since $J_0(bx)$ would bring an oscillatory character to the integrand and cause the numerical quadrature to be hard to perform. A six-point Gauss–Legendre quadrature in each of the following intervals (0., 1.0), (1.0, 2.0), and (2.0, 3.0) has been found satisfactory for our accuracy requirements. This approach gave us six significant figures for values of s_2^{mn} (in units of a) ranging from 0.001 to a value close to unity $(s_z^{mn} = 0.999)$. The function $J_{i0}(3b)$,

$$J_{i0}(3b) = \int_{3b}^{\infty} \frac{du}{u}\, J_0(u), \quad (17)$$

is easily evaluated using an expression in term of Chebyshev polynomials (see [13, p. 325, Table 9.3]). In practice, when a good choice between Eqs. (2), (3), and (14)

is made according to the actual value of s_2^{mn}, a sensible way for evaluating accurately and at moderate cost the Madelung summations arising in quantum-mechanical calculations of chainlike systems has been achieved.

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