Theor Chim Acta (1988) 73: 229-232

Theoretica Chimica Acta

Electrostatic sums for polymer chains*

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(Received February 9, revised July 17/Accepted July 31, 1987)

A rapidly convergent expression is given for calculating the Madelung energy of infinite linear polymers with small radius.

Key words: Electrostatic energy — Polymer chain

1. Introduction

The electrostatic or Madelung energy is an important contribution to the total energy of any extended chemical system. For infinite chains, the sums representing these terms are only conditionally convergent, so that direct evaluation is impractical, and much attention has been devoted to finding alternative methods for computing them [1-4]. If cylindrical coordinates are used, with the axis directed along the chain, the essential parameters entering into these sums are the radial and axial coordinate differences for pairs of inequivalent sites within a unit cell. If we denote such differences by α and β, respectively, then the basic electrostatic sum has the form

$$S(\alpha, \beta) = \sum_{n=1}^{\infty} \left\{ \frac{1}{\sqrt{\alpha^2 + (n+\beta)^2}} - \frac{1}{n} \right\}. \tag{1}$$

For large values of α we have Riemann's identity

$$\sum_{n=-\infty}^{\infty}{}' \left\{ \frac{1}{\sqrt{\alpha^2 + (n+\beta)^2}} - \frac{1}{n} \right\} = 4 \sum_{k=1}^{\infty} \cos(2\pi k\beta) K_0(2\pi k\alpha) + 2[\ln(\alpha/2) - \gamma] - 1/\sqrt{\alpha^2 + \beta^2} \tag{2}$$

* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

obtained by means of the Poisson summation formula. The sum on the right hand side is exponentially convergent and for $\alpha > 1$, since the Bessel function can be replaced by its asymptotic approximation, this series is easily implemented on a programmable calculator. In practice, the numerical schemes devised for dealing with (1) experience the most difficulty when α is small. The purpose of this note is to present a rapidly convergent resummation of $S(\alpha, \beta)$ to deal with this case

2. Theory

We begin with a sequence of elementary transformations:

$$S(\alpha,\beta)=\sum_{n=1}^{\infty}\{[(n+\beta)^2+\alpha^2]^{-1/2}-(n+\beta)^{-1}\}+\sum_{n=1}^{\infty}\{(n+\beta)^{-1}-n^{-1}\}$$

$$=-\gamma-\psi(1+\beta)-\sum_{n=1}^{\infty}\int_0^{\alpha}\frac{u\,du}{[(n+\beta)^2+u^2]^{3/2}}$$

$$=-\gamma-\psi(1+\beta)-\alpha^2\int_0^1 u\phi(\alpha)\,du. \tag{3}$$

Here, γ is Euler's constant, ψ is the logarithmic derivative of the gamma function [5], and

$$\phi(\alpha)=\sum_{n=1}^{\infty}[(n+\beta)^2+u^2\alpha^2]^{-3/2} \tag{4}$$

The Mellin transform of $\phi(\alpha)$ is

$$\Phi(s)=\pi^{-1/2}u^{-s}\Gamma(s/2)\Gamma(3/2-s/2)\zeta(3-s,\beta+1),\qquad (0<\operatorname{Re} s<2) \tag{5}$$

where $\zeta(z, v)$ is the generalized Riemann-Zeta function [6]. Therefore, by the Mellin inversion formula, we have the integral representation

$$\phi(\alpha)=\pi^{-1/2}\int_{c-i\infty}^{c+i\infty}(u\alpha)^{-s}\Gamma(s/2)\Gamma(3/2-s/2)\zeta(3-s,\beta+1)\frac{ds}{2\pi i}\qquad (0<c<2). \tag{6}$$

Next, by inserting (6) into (3), we have an apparently new integral representation for $S(\alpha, \beta)$:

$$S(\alpha,\beta)=-\gamma-\psi(1+\beta)+\pi^{-1/2}\int_{c-i\infty}^{c+i\infty}\frac{du}{2\pi i}u^{-1}\alpha^{-u}\Gamma(1+u/2)\Gamma(1/2-u/2)\times\zeta(1-u,\beta+1)\qquad (-2<c<0). \tag{7}$$

The singularities in the integrand in (7) are a double pole at $u=0$, and two sequences of simple poles: $u=-2(k+1)$, $u=2k+1$; $k=0, 1, 2, \ldots$. When $0 \le \alpha < 1$ the integrand decays exponentially away from the negative real axis in the left hand plane, so by Jordan's lemma we can close the contour by an infinite semi-circle and express the integral in terms of the residues at the first sequence of simple poles. This gives our principal result

$$S(\alpha, \beta) = -\gamma - \psi(1+\beta) - \sum_{k=1}^{\infty} (-1)^{k+1} \frac{(2k)!}{(k!)^2} \zeta(2k+1, \beta+1)(\alpha/2)^{2k}. \tag{8}$$

Equation (8) can also be derived by expanding the series in (4) in powers of α and integrating term by term as indicated in (3). However, the approach we have used is very powerful and provides asymptotic expansions quickly in similar cases where elementary methods cannot be used.

For $\alpha > 1$, the integrand decays off the real axis into the right hand u-plane; however, in this case the rate of decay is only algebraic and not sufficient that the contribution to the integral from the neighborhood of infinity can be neglected. Indeed, if the contour is closed as before by a large semi-circle into the right hand plane, the residue sum gives precisely the non-exponential terms corresponding to the right hand side of (2).

The Riemann-zeta functions appearing in (8), which are essentially higher derivatives of the gamma function, are known exactly for rational values of β and have been extensively tabulated in other cases (see, e.g., the eighty place tables given by Fransen and Wrigge [7]). As an illustration of the utility of (8) we have calculated $S(\alpha, \beta)$ using a pocket calculator for $\beta = 0$, $1/2$ (by symmetry, only the range $-1/2 < \beta \leq 1/2$ need be considered). In Table 1, we also give the number of terms in (8) needed to give nine place accuracy. In these cases (8) reduces to

$$\begin{aligned} S(\alpha, 0) &= (1+\alpha^2)^{-1/2} - 1 + T(\alpha/2) \\ S(\alpha, 1/2) &= 2 \ln(2/e) - S(\alpha, 0) + 2T(\alpha), \end{aligned} \tag{9}$$

where

$$T(\alpha) = \sum_{k=1}^{\infty} (-1)^k \frac{(2k)!}{(k!)^2} [\zeta(2k+1) - 1]\alpha^{2k} \equiv \sum_{k=1}^{\infty} (-1)^k B_k \alpha^{2k}, \tag{10}$$

which converges much faster. For convenience we record the coefficients B_k in Table 2.

Table 1. Selected values of $S(\alpha, \beta)$ calculated from (8). N denotes the number of terms necessary for nine place accuracy

α	$S(\alpha, 0)$	$S(\alpha, 1/2)$	N
0	0	−0.613705639	0
0.02	−0.000240349	−0.613788510	2
0.04	−0.000960651	−0.614037020	3
0.05	−0.001500146	−0.614223297	3
0.06	−0.002158678	−0.614450853	3
0.08	−0.003820737	−0.615029496	3
0.10	−0.005971712	−0.615772221	4
0.15	−0.013329806	−0.618340351	5
0.20	−0.023438471	−0.621907938	6

Table 2. Coefficients appearing in expressions (9), (10)

k	B_k
1	0.404113806
2	0.221566531
3	0.166985548
4	0.140587496
5	0.124535527
6	0.113387089
7	0.104978702
8	0.098290764
9	0.092776684
10	0.088110136

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