Impurities in S=1/2 Heisenberg Antiferromagnetic Chains: Consequences for Neutron Scattering and Knight Shift

Sebastian Eggert$^a$, Ian Affleck$^b$

$^a$ Theoretical Physics, Chalmers University of Technology, and Göteborg University, 41296 Gothenburg, Sweden and $^b$Canadian Institute for Advanced Research and Physics Department University of British Columbia, Vancouver, B.C., V6T 1Z1, Canada

(November 11, 2018)

Abstract

Non-magnetic impurities in an S=1/2 Heisenberg antiferromagnetic chain are studied using boundary conformal field theory techniques and finite-temperature quantum Monte Carlo simulations. We calculate the static structure function, $S_{\text{imp}}(k)$, measured in neutron scattering and the local susceptibility, $\chi_i$ measured in Knight shift experiments. $S_{\text{imp}}(k)$ becomes quite large near the antiferromagnetic wave-vector, and exhibits much stronger temperature dependence than the bulk structure function. $\chi_i$ has a large component which alternates and increases as a function of distance from the impurity.

75.10.Jm, 75.20.Hr
Although the spin chain problem has been a popular topic for theoretical physicists since the early days of quantum mechanics, the correlation functions of the antiferromagnetic Heisenberg spin-1/2 chain could only be calculated with the help of modern quantum field theory [1]. Adding non-magnetic impurities to a spin-chain compound breaks the chains up into finite sections with essentially free boundary conditions. The correlation functions in the presence of such a boundary were calculated only rather recently [2]. These results provide a simple application of a general theory of conformally invariant boundary conditions which has been applied to a wide variety of quantum impurity problems in condensed matter and particle physics [3]. These functions exhibit a universal dependence on the boundary, at long distances and times. In this paper we wish to focus on a couple of applications of these results of experimental relevance: the impurity contribution to the static structure function, $S_{\text{imp}}(k, T)$, and the local susceptibility, $\chi_i(T)$. We derive analytic expressions for these quantities using field theory methods and compare them with finite-T Monte Carlo simulations using lengths of up to $l = 128$ with a varying number of time-steps up to 64 and several hundred thousand sweeps through each lattice.

The Heisenberg Hamiltonian for the antiferromagnetic spin-1/2 chain

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}$$  \hspace{1cm} (1)

is equivalent to a free boson field theory in (1+1) dimensions in the low energy, long-distance limit [4]. The spin operators are expressed in terms of the boson $\phi$ as

$$S^z_j \approx \partial_x \phi/\sqrt{2\pi} + a(-1)^j \cos \sqrt{2\pi} \phi, \hspace{1cm} (2)$$

where $a$ is a constant. The boson Hamiltonian is then simply given by the free part together with terms which become irrelevant as the temperature is lowered. Those irrelevant terms give rise to temperature and finite length dependent corrections with a characteristic power-law.

This theory has been used successfully to calculate impurity effects [2], the low energy spectrum [3], and correlation functions [1]. The latter agree well with recent neutron-scattering experiments [6]. Like the expression for the spin operators in equation (2), the correlation functions also acquire an alternating and a uniform part as a function of the site index $x$. At finite-temperature, the alternating part is given by:

$$<S^z(x, t_1)S^z(y, t_2)>_{\text{alt}} \rightarrow c \frac{(-1)^{x-y}}{v^{\beta} \sqrt{\sinh \frac{\pi(x-y-\nu \Delta t)}{v^{\beta}} \sinh \frac{\pi(x-y+\nu \Delta t)}{v^{\beta}}}} (3)$$

($\Delta t \equiv t_2 - t_1$). We set the lattice spacing to 1. The spin-wave velocity is known to be $v = J \pi/2$ from the Bethe-ansatz. The constant $c$ can be determined numerically and is given by $c = a^2/2$ times an arbitrary normalization of the two-point function, which we chose to set to one. The irrelevant terms in the Hamiltonian give logarithmic corrections to this expression [4]. In fact, it has been shown recently that the logarithmic corrections give rise to an infinite slope of the uniform susceptibility at zero temperature [7].

The correlation functions in the presence of a boundary were first calculated in reference [2]. There it was argued that the free boundary condition on the spin operators corresponds,
in the continuum limit, to a boundary condition on the bosons: \(\phi(0) = \phi_L(0) + \phi_R(0) = \sqrt{\pi/8}\). Since \(\phi_L\) is a function only of \(vt + x\) and \(\phi_R\) of \(vt - x\), this implies that we may simply regard this boundary condition as defining \(\phi_R\) to be the analytic continuation of \(\phi_L\) to the negative axis \(\phi_R(x) = -\phi_L(-x) + \sqrt{\pi/8}\). Whereas the bulk correlation function factorizes into a product of left and right 2-point Green’s functions, the boundary correlation function becomes a 4-point Green’s function for left-movers. Consequently, while the uniform part is largely unaffected by an open boundary condition, the alternating part gets modified to

\[
c (\pi/v\beta)^{3/2} <S^z(x)S^z(y)> e^{-ik(x-y)} \xrightarrow{l \to \infty} \left[ S(k) + S_{\text{imp}}(k) \right].
\]

The structure function for the finite chains has been decomposed into a “bulk” part \(S(k)\) which is independent of length and an “impurity” part of order \(1/l\):

\[
S_{\text{imp}}(k) \equiv \lim_{l \to \infty} [S_l(k) - S(k)].
\]

The bulk part reproduces the signal of a system without open ends (e.g. an infinite chain) while the effect of the open boundary condition is entirely contained in the impurity part. Higher order \(O(1/l^2)\) terms will also be present, but can be neglected if the impurities are dilute. Since each impurity creates the same contribution \(S_{\text{imp}}(k)\) in the dilute limit, the experimental signal will contain the impurity part as a term which scales with impurity concentration \(n\) to first order:

\[
S_{\text{exp}}(k) \approx S(k) + nS_{\text{imp}}(k).
\]

From the results of equations (3) and (4), it is clear that we expect interesting effects for wave-vectors near \(k \approx \pi\). Field theory predictions for small \(k - \pi\) and \(T\) are obtained by Fourier transforming equations (3) and (4). We assume here that the impurities are dilute enough so that the infrared cut-off is always given by the inverse temperature \(\beta \ll l/v\). The bulk structure function (3) can then be expressed in terms of the digamma function \(\psi\) and the reduced variable \(k' \equiv (k - \pi)v\beta/\pi\):

\[
S(k') = 2c \left[ \ln(\Lambda\beta J) - \Re \psi(1/2 - ik'/2) \right],
\]
where $\Lambda$ is a constant depending on the cut-off.

The impurity contribution, $S_{\text{imp}}(k')$ is obtained by Fourier transforming equation (4) with the bulk part, from equation (3), subtracted off assuming two open ends. This subtraction eliminates the ultra-violet divergence, giving the scaling form:

$$S_{\text{imp}}(k') = \frac{2v\beta}{\pi} \int_{0}^{\infty} dw \left[ \int_{0}^{w} du \frac{\cos k'u}{\sinh u} \left( \sqrt{1 - \frac{\sin^2 u}{\sinh^2 w}} - 1 \right) - \int_{w}^{\infty} du \frac{\cos k'u}{\sinh u} \right]$$

$$= v\beta f(k') \quad (9)$$

Here $u = \pi(x - y)/v\beta$, $w = \pi(x + y)/v\beta$. Note that, apart from the logarithmic term in equation (8), $S(k')$ and $S_{\text{imp}}(k')$ are functions only of the scaling variable $k' = (k - \pi)v\beta/\pi$, but we expect corrections to this scaling behavior from irrelevant operators and the ultraviolet cut-off which become smaller as $T \to 0$ and $k - \pi \to 0$ with $k'$ held fixed. For small $k'$ we have $S(k') \propto \ln(\beta) + \text{const.} + \mathcal{O}(k'^2)$ and $S_{\text{imp}}(k') \propto v\beta[\text{const.} + \mathcal{O}(k'^2)]$, so that the impurity part has a much stronger temperature dependence. The second term in equation (9) can be written

$$\int_{0}^{\infty} dw \int_{w}^{\infty} du \frac{\cos k'u}{\sinh u} = -\frac{4}{v\beta} \text{Im} \psi(1/2 - ik'/2),$$

which is the dominant contribution for small $k'$. At large $k'$, however, the leading behavior comes from the first integral $S_{\text{imp}}(k') \to -v\beta c/\pi k'^2$, while $S(k')$ vanishes exponentially. (In the opposite limit $l/v \ll \beta \to \infty$ we get a delta-function at $k = \pi$ for both the impurity and the bulk contributions $S_{\text{imp}}(k = \pi) \propto l$ and $S(k = \pi) \propto \ln(l)$.)

Our Monte Carlo results for $S(k)$ and $S_{\text{imp}}(k)$ are shown in figures (1) and (2) for four temperatures. Note, that since the impurity part scales with the inverse temperature $\beta$, it may make a sizable contribution even at moderate impurity densities. To show the predicted scaling form we plotted the results as a function of the reduced variable $k'$ in figures (3) and (4). The Monte Carlo simulations agree reasonably well with the field theory predictions. This comparison with the Monte Carlo data was used to extract the constant $c = 0.14$ and $\Lambda = 0.75$ in equation (8).

We now consider the local susceptibility $\chi_i$ at any arbitrary site $i$ under the influence of a uniform magnetic field $h$ acting on the complete chain

$$\chi_i(T) \equiv \frac{\partial}{\partial h} < S_i^z > |_{h=0} = \frac{1}{T} \sum_j < S_j^z S_i^z >, \quad (10)$$

For a chain with periodic boundary conditions, $\chi_i$ is the same for all sites because of translational invariance.

If we are dealing with an open boundary condition, however, the translational invariance is clearly broken and we would naively expect the open end to be more susceptible. Moreover, it is now possible, in the field theory treatment, to have a non-zero alternating susceptibility as a function of site index $\chi_x = \chi_x^{\text{uni}} + (-1)^x \chi_x^{\text{alt}}$. Using the analytic continuation of the left-movers onto the negative half axis from above, $\chi_x^{\text{alt}}$ is given by a non-zero three point Green’s function:

$$\chi_x^{\text{alt}} \equiv \beta < S_x^{\text{alt}} (x) \int dy S_{\text{uni}}^z (y) >$$

$$= \frac{a\beta}{\sqrt{8\pi}} \int_{-\infty}^{\infty} dy \left( ie^{-i\sqrt{2}\phi_L(x,t')} e^{i\sqrt{2}\phi_L(x-t')} \frac{\partial \phi_L}{\partial x} (y, t) + h.c. \right)$$
\[
\frac{a \beta}{4 \pi} \int_{-\infty}^{\infty} dy \frac{v \beta}{\pi} \sinh \frac{\pi}{v \beta} (y + x + iv \Delta \tau) \sqrt{\frac{\sinh \frac{2 \pi x}{v \beta}}{\sinh \frac{2 \pi x}{v \beta}}} (y - x + iv \Delta \tau) \rightarrow a \frac{v}{\sqrt{\pi}} \sqrt{x}
\]

where \(x\) is the distance from an open boundary condition. At low temperatures the alternating part actually increases with the distance \(\sqrt{x}\) from the open end. Any finite temperature suppresses this growth exponentially with \(x\), so that we expect a typical maximum which gets shifted further into the chain as the temperature is lowered. Furthermore, even at \(T = 0\), the staggered magnetization does not increase indefinitely with distance from the impurity, but rather oscillates with a wavelength, \(4\pi v/h\), i.e.

\[
M_{\text{alt}}(x, h, T = 0) = a \sqrt{\frac{2}{x}} \sin(\frac{hx}{2v}).
\]

This exotic behavior is similar to Friedel oscillations except that the \(1/r^3\) decay which occurs there gets enhanced to a \(\sqrt{r}\) growth due to a combination of reduced dimensionality and the absence of charge fluctuations in this pure spin system.

The result from equation (11) can be confirmed independently with quantum Monte Carlo simulations. The local susceptibility as a function of distance from the open end is shown in figure (5) from Monte Carlo simulations at \(T = J/15\). After extracting the uniform and alternating parts as shown in figure (6), we can compare the alternating part to the predicted form from equation (11) where the overall constant was chosen to be \(a = 0.58\). The field theory prediction \(c = a^2/2\), together with the value \(c = 0.14\) from our MC measurement of \(S(k)\) gives \(a \approx 0.53\) in reasonable agreement. While the shape of the theoretical prediction for \(\chi_{\text{alt}}\) fits the Monte Carlo results very well, there is an unexplained shift of about two sites, which might be due to irrelevant operators. The functional dependence in equation (11) holds rather well for all temperatures \(\beta\) sampled (up to the shift of two sites). For \(T = J/15\) the shift in the susceptibility due to the impurity is larger than the bulk susceptibility over a distance of about 25 lattice sites from the impurity. Thus we expect that it should be possible to observe this effect in nuclear magnetic resonance Knight shift experiments. Note, that \(\chi_i < 0\) for small even \(i\), so that those spins will tend to anti-align with the applied field.

The uniform part of the susceptibility is not directly affected by the boundary condition, but gets an additional non-universal contribution near \(x = 0\) from an irrelevant boundary operator \([2,8]\), which also appears to be present in the Monte Carlo results in figure (6). This shift in the uniform susceptibility is what would be expected classically, but the large alternating part is a purely quantum mechanical effect.

In conclusion, we have calculated the effect of impurities on the neutron-scattering cross-section and the NMR Knight shift using both field theory and Monte Carlo methods. The two methods are in reasonable agreement and the effects seem large enough to be observable experimentally. The Knight shift actually increases with distance from the impurity in the limit of zero field and temperature.

ACKNOWLEDGEMENTS
We would like to thank Bill Buyers, Junwu Gan, Henrik Johannesson, Rob Kiefl, Erik Sørensen and Eugene Wong for helpful discussions. This research was supported in part by NSERC of Canada and the Swedish Natural Science Research Council.
REFERENCES

[1] A. Luther, I. Peschel, Phys. Rev. B12, 3908 (1975).
[2] S. Eggert, I. Affleck, Phys. Rev. B46, 10866, (1992).
[3] I. Affleck, Correlation Effects in Low-Dimensional Electron Systems (ed. A. Okiji, N. Kawakami, Springer-Verlag, Berlin 1994), p. 82.
[4] For a review of the conformal field theory treatment of the spin-1/2 chain and earlier references see I. Affleck, Fields, Strings and Critical Phenomena (ed. E. Brézin, J. Zinn-Justin North-Holland, Amsterdam 1990), p.563.
[5] I. Affleck, D. Gepner, H.J. Schulz, T. Ziman, J. Phys. A22, 511, (1989).
[6] D.A. Tennant, T.G. Perring, R.A. Cowley, S.E. Nagler, Phys. Rev. Lett. 70, 4003 (1993).
[7] S. Eggert, I. Affleck, M. Takahashi, Phys. Rev. Lett. 73, 332 (1994).
[8] S. Eggert, “Impurity Effects in Antiferromagnetic Quantum Spin-1/2 Chains”, Ph.D. Thesis, University of British Columbia, Vancouver, August 1994.
[9] H.J. Schulz, Phys. Rev. B34, 6372 (1986).
[10] M. Abramowitz and I. A. Stegun Handbook of Mathematical Functions (Dover, New York, 1964).
FIGURES

FIG. 1. The bulk structure factor $S(k)$ according to quantum Monte Carlo simulations.

FIG. 2. The impurity part of the structure factor $S_{\text{imp}}(k)$ according to quantum Monte Carlo simulations.

FIG. 3. Monte Carlo results for the shifted bulk structure function, $S(k') - 2c \ln(\Lambda J/\beta)$ compared to the field theory prediction of equation (8), with $c = 0.14$ and $\Lambda = 0.75$.

FIG. 4. Monte Carlo results for the scaled impurity part $T S_{\text{imp}}(k')$ compared to equation (9) with $c = 0.14$.

FIG. 5. The local susceptibility vs. distance from the open end according to Monte Carlo simulations at $T = J/15$.

FIG. 6. The uniform and alternating parts of the local susceptibility according to Monte Carlo simulations at $T = J/15$ compared to the field theory equation (11) with $a = 0.58$. 
FIG. 1. The bulk structure factor $S(k)$ according to quantum Monte Carlo simulations.

FIG. 2. The impurity part of the structure factor $S_{\text{imp}}(k)$ according to quantum Monte Carlo simulations.
FIG. 3. Monte Carlo results for the shifted bulk structure function, $S(k') = 2c \ln(\Lambda J/\beta)$ compared to the field theory prediction of equation (8), with $c = 0.14$ and $\Lambda = 0.75$.

FIG. 4. Monte Carlo results for the scaled impurity part $T S_{\text{imp}}(k')$ compared to equation (9) with $c = 0.14$. 

2
FIG. 5. The local susceptibility vs. distance from the open end according to Monte Carlo simulations at $T = J/15$.

FIG. 6. The uniform and alternating parts of the local susceptibility according to Monte Carlo simulations at $T = J/15$ compared to the field theory equation (11) with $a = 0.58$. 
