Exact Analysis of ESR Shift in the Spin-1/2 Heisenberg Antiferromagnetic Chain

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A systematic perturbation theory is developed for the ESR shift and is applied to the spin-1/2 Heisenberg antiferromagnetic chain with a general anisotropic exchange interaction. Using the Bethe ansatz technique, the resonance shift is obtained exactly for the whole range of temperature and magnetic field, in the first order of the anisotropy. The obtained g-shift strongly depends on magnetic fields at low temperature, showing a significant deviation from the previous classical result.

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Many of the interesting phenomena and experimental measurements in strongly correlated quantum systems are related to dynamics of the system. Despite the considerable progress in many-body theory, available exact results on quantum dynamics in many-body systems are still rather scarce. Indeed, even a systematic framework for approximate calculations is often not well established.

Electron spin resonance (ESR) is a typical example of such dynamical phenomena. Electron spin resonance frequency is the Zeeman term, and hence rather much remains open in ESR theory. The ESR shift \( \delta \omega \) is usually defined as the deviation of the resonance frequency from the paramagnetic resonance frequency \( \omega = H \). Nagata-Tazuke theory \( \delta \omega \) published more than 30 years ago has been the only theory for arbitrary temperature, and still remains the standard. However, it is based on the classical spin approximation and does not incorporate the quantum fluctuation. In this letter, we utilize the integrability of the spin-1/2 Heisenberg antiferromagnetic chain to go beyond the limitations of the previous approaches. As a result, we obtain the ESR shift for general anisotropic interactions at arbitrary temperature and magnetic field, fully including the quantum effects.

Nagata-Tazuke theory \( \delta \omega \) is based on the fundamental formula for the ESR shift, first proposed in ref. \( \delta \omega \). Its simplest form reads:

\[
\delta \omega = \frac{\langle [A, S^-] \rangle}{2(S_z^2)}
\]

where \( \langle \cdots \rangle \) is the thermal expectation value with respect to \( \mathcal{H} \), and \( A \equiv [\mathcal{H}', S^+] \). In ref. \( \delta \omega \), this formula is further evaluated for the 1D classical Heisenberg antiferromagnet in the lowest order of \( \mathcal{H} \), utilizing Fisher’s solution \( \delta \omega \) of the classical Heisenberg chain. Owing to the reliance on the classical limit, we cannot expect their result to apply to the strongly quantum system. On the other hand, as some nontrivial assumptions are involved in the original derivation of the formula \( \delta \omega \), in literatures there seems to be a confusion over the validity of the starting point, eq. \( \delta \omega \) itself.

Here, we clarify the validity and limitation of the formula \( \delta \omega \). To discuss the resonance shift unambiguously, in this letter, we define the shift \( \delta \omega_{\sigma \sigma} \) for the polarization \( \sigma \) in terms of the dynamical susceptibility as

\[
\delta \omega_{\sigma \sigma} = \frac{\int_0^\infty d\omega \chi''_{\sigma \sigma}(\omega)}{\int_0^\infty d\omega \chi''_{\sigma \sigma}(\omega)} - H.
\]
Note that the integration interval is taken to be $[0, \infty]$ instead of $[-\infty, \infty]$, because $\chi''_{\mu}(\omega)$ is an odd function of $\omega$. By using a sum rule $\mathbf{3}$, the numerator of eq. $\mathbf{4}$ is explicitly written as $-\pi([\mathcal{H}, S^z], S^z)/2$. In contrast, the integration in the denominator cannot be performed analytically. Hence we shall evaluate $\mathbf{4}$ perturbatively.

The computation in the first order can be carried out without resorting to any other approximation, by utilizing the exact Heisenberg equation of motions such as $\dot{S}^z = -i[H S^z + iA \mathbf{3}]$. After straightforward but somewhat tedious calculations, we obtain the first order perturbative contribution to eq. $\mathbf{4}$, exactly as in eq. $\mathbf{3}$. Namely, eq. $\mathbf{3}$ is generally exact in the first order of the anisotropic perturbation $\mathcal{H}'$. Note that, however, eq. $\mathbf{3}$ breaks down in the second and higher orders in $\mathcal{H}' \mathbf{2}, \mathbf{5}$. Restricting eq. $\mathbf{3}$ to the first order in $\mathcal{H}'$, we obtain the simplified expression

$$\delta \omega_{\sigma \sigma} = -\frac{\langle [A, S^z] \rangle_0}{2\langle S^z \rangle_0} + O(\mathcal{H}^2),$$

where $(\cdots)_0$ is the thermal expectation value with respect to the unperturbed term $\mathcal{H}_0 = \mathcal{H}_{SU(2)} + \mathcal{H}_Z$.

As there is no contribution to $\mathbf{6}$ from satellite peaks $\mathbf{2}$, it exactly gives the shift of the main paramagnetic resonance in the first order. As we will see, for the exchange anisotropy (e.g. dipolar interaction), the first order contribution is generally non-vanishing. Thus the precise evaluation of eq. $\mathbf{6}$ is of great importance.

Now, let us consider the Heisenberg chain

$$\mathcal{H}_0 = \mathcal{H}_{SU(2)} + \mathcal{H}_Z = J \sum_{j=1}^N S_j \cdot S_{j+1} - H \sum_{j=1}^N S_j^z,$$

with a small anisotropic interaction as a perturbation $\mathcal{H}'$. As $\mathcal{H}'$, we consider the anisotropic exchange interaction. Since the antisymmetric exchange interaction (Dzyaloshinskii-Moriya interaction) does not contribute in the first order, we only consider the symmetric (with respect to an exchange of neighboring spins) exchange interaction. The dipolar interaction may also be approximated by a suitable exchange anisotropy in the nearest neighbor interaction. Assuming the chain is uniform, the anisotropic exchange interaction can always be diagonalized as

$$\mathcal{H}' = \sum_j \sum_{p,q \in \{a,b,c\}} J'_{pq} S_j^p S_{j+1}^q, \quad J'_{pq} = J'_{p} \delta_{pq},$$

where $a, b, c$ are the principal axes of the anisotropy. Let the direction of the static magnetic field $H$ be $(\alpha, \beta, \gamma) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ in the $(a, b, c)$-coordinate, where $\theta$ is zenith angle and $\phi$ is azimuth angle. As introduced previously, the $(x, y, z)$-coordinate is defined so that $H$ is applied in the $z$-axis. The resonance shift $\mathbf{5}$ is now evaluated as

$$\delta \omega = f(\theta, \phi) \times Y(T, H).$$

Here the direction-dependent factor $f(\theta, \phi)$ and the field- and temperature-dependent factor $Y(T, H)$ are respectively given by

$$f(\theta, \phi) = J'_f(1 - 3a^2) + J'_f(1 - 3b^2) + J'_f(1 - 3c^2), \quad Y(T, H) = \frac{\langle S_j^z S_{j+1}^z - S_j^z S_{j+1}^z \rangle_0}{\langle S_j^z \rangle_0},$$

In general, eqs. $\mathbf{3}, \mathbf{5} - \mathbf{10}$ are valid for arbitrary spin, when we consider $\mathcal{H}'$ as a perturbation. It would be interesting to evaluate them numerically, for example by a Quantum Monte Carlo simulation. However, this could be a challenging problem especially in the weak field regime; there will be a cancellation of significant digits in taking the difference between the very close quantities $\langle S_j^z S_{j+1}^z \rangle$ and $\langle S_j^z S_{j+1}^z \rangle$.

Hereafter we shall concentrate on the $S = 1/2$ case. The total Hamiltonian $\mathbf{2}$ is no longer integrable even with $S = 1/2$, due to the existence of the anisotropy $\mathbf{4}$ and magnetic fields. The first-order shift $\mathbf{10}$, however, can be exactly calculated by the Bethe ansatz technique $\mathbf{10}$ utilizing the integrability of the zeroth order Hamiltonian $\mathbf{3}$. After long calculations, we obtain

$$Y(T, H) = \frac{1}{2} - \frac{T}{2nJ} \int_{-\Gamma} \ln (1 + \eta(x + i)) \, dx,$$

where the contour $\Gamma$ encloses the real axis counterclockwise: for instance $\Gamma$ can be the rectangular contour whose corners are $-\infty - i, +\infty - i, +\infty + i$, and $-\infty + i$.

The unknown function $\eta(x)$ is determined by the following non-linear integral equation:

$$\ln \eta(x) = \frac{2\pi J}{T} a_1(x) - \frac{H}{T} - \int_{-\Gamma} a_2(x - y - i) \ln(1 + \eta(y + i)) \, dy,$$

where $a_n(x) = n!(\pi x^2 + n^2)$.

Although the result $\mathbf{10}$ is limited only to the $S = 1/2$ Heisenberg antiferromagnetic chain, it gives the resonance shift $\mathbf{10}$ without the difficulty due to the cancellation of significant digits. As a consequence, the resonance shift can be evaluated numerically with a very high accuracy for arbitrary fields and temperatures.

In experimental studies, it is customary to discuss the shift in terms of the effective $g$-factor

$$g_{ef} \equiv g_\infty \left(1 + \frac{\delta \omega}{H}\right) = g_\infty \left(1 + \frac{f(\theta, \phi)Y(T, H)}{H}\right),$$

and the $g$-shift $\Delta g \equiv g_{ef} - g_\infty$. Here $\delta \omega$ is the frequency shift we have obtained with setting $\mu_B g_\infty = 1$, and $g_\infty$ is the $g$-factor appearing in the Zeeman term. When $J'_{p} \ll J, H$, we can identify $g_\infty$ with the observed $g$-factor in the high temperature limit.

In Fig. $\mathbf{1}$ the temperature dependence of $JY(T, H)/H$, which is proportional to the $g$-shift $\Delta g$, is depicted for
various magnetic fields. We find that $\Delta g$ clearly depends on the magnetic fields $H$ especially in the low-temperature regime, and converges to a certain value at $T = 0$ for any finite $H$. One also finds that $\Delta g$ decreases with increasing $H$. In the limit $H \to \infty$, $\Delta g$ vanishes at any temperature. In contrast, for a weak magnetic field $H \ll 1$, $\Delta g$ logarithmically increases with decreasing temperature and approaches infinity when $H \to 0$.

In Fig. 1 the present results are compared to the previous classical result \[10\], as well as for the classical result does not describe the $H$-dependence as it is obtained in the lowest order expansion in $H$.

Comparing the integral equations \[10\] and \[12\] for $Y(T, H)$ and that for the magnetization $(S^z)_0$ in the $S = 1/2$ Heisenberg chain \[6\], we find a remarkable identity relating them:

$$Y(T, H) = \frac{1}{J} \int \langle S_j^z \rangle_0 dJ.$$  \tag{15}$$

This is useful in obtaining the low-temperature asymptotics of the shift. Because the low-temperature asymptotics of $\langle S_j^z \rangle_0$ is derived by an effective field theory \[12\], we obtain, for $H \ll T \ll J$,

$$Y(T, H) = \frac{H}{J \pi^2} \left\{ \mathcal{C} + \frac{1}{2} \ln \mathcal{L} + \frac{1}{4 \mathcal{L}} + \frac{\ln \mathcal{L}}{4 \mathcal{L}} - \frac{\sqrt{3} T^2}{2 J^2 \pi} + C \right\},$$  \tag{16}$$

where $\gamma_E$ is the Euler constant, and the integration constant $C \sim 3/4$ is determined by the fitting to the exact result eq. \[14\], as in Fig. 2.

Note that the leading log in \[16\] agrees exactly to what was obtained in ref. \[3\] via a field theoretical approach. However, the “leading log” is only dominant in an extremely low temperature and magnetic field. For a realistic parameter regime, the subleading (in $J/T$ or $J/H$) corrections determined in the present study is actually essential in a quantitative discussion of the shift.

Furthermore, our analysis determines the running coupling constant with respect to a marginal operator in ref. \[2\] precisely. Following the logic of ref. \[2\], this allows a prediction of the linewidth $\kappa$ including the subleading corrections for $J' \neq 0, J'_a = J'_b = 0$:

$$\kappa = \frac{\epsilon T}{\pi^3} \left( \frac{J'}{J} \right)^2 \left\{ \mathcal{C} + \frac{1}{2} \ln \mathcal{L} + \frac{1}{4 \mathcal{L}} + \frac{\ln \mathcal{L}}{4 \mathcal{L}} + C \right\}^2,$$  \tag{17}$$

where $\epsilon = 4$ ($\epsilon = 2$) when the applied field $H$ is parallel (perpendicular) to the $c$-axis. The subleading corrections should also be essential in a quantitative prediction for realistic values of temperature and magnetic field.

Finally, we discuss experimental data in the light of our results. In Fig. 3 we analyze the $g$-shift data on LiCuVO$_4$, which is considered to be an $S = 1/2$ Heisenberg antiferromagnetic chain. The data are taken from ref. \[13\] (powder sample) and ref. \[14\] (single crystal). We take the estimate $J = 44$ [K] from ref. \[13, 15\] for...

**Fig. 1:** The temperature dependence of $JY(T, H)/H$ for various $H$. For comparison, the result from the classical approximation is also depicted. Inset: details of the low-temperature...

**Fig. 2:** Comparison of the exact result with the asymptotic behavior \[16\] (we set $C = 3/4$). A crossover from a regime dominated by logarithmic corrections to a regime dominated by algebraic corrections occurs at $T \sim H$. 
anisotropic exchange

Effective

Then obtained for each set of experimentally observed

in the magnetic field

regime in which we discuss the experimental data.

The principal axes of the $g$-tensor, i.e. $(g^a, g^b, g^c)$ and

those of the anisotropic exchange tensor \[^7\] are thought
to coincide with the crystallographic axes $(a, b, c)$ \[^13\] \[^14\]. Therefore, we use the bare $g$-factor $g_{bc}^{a,b,c}$ and the

anisotropic exchange $J'_{a,b,c}$ for each crystallographic axis

as fitting parameters. Here we note that we can set one

of $J'_{a,b,c}$ to zero, by renormalizing the isotropic exchange $J$. The normalized $g$-shift corresponding to $Y(T, H)$ was then obtained for each set of experimentally observed
effective $g$-factor, using eqs. \[^11\] and \[^10\].

In ref. \[^13\], the anisotropy in $ab$-plane was neglected

in analyzing the powder sample. For this set of data, we

obtain $g_{bc}^a = 2.22$, $g_{bc}^b = 2.09$ as a result of fitting in

Fig. \[^3\]. The best fit value of the anisotropic exchange was

$J'_c \sim -0.15 J$ for $H \parallel c$ and $J'_c \sim -0.11 J$ for $H \perp c$, where we set $J'_a = J'_b = 0$. For the data from ref. \[^14\], our fitting

yields $g_{bc}^c = 2.31, g_{bc}^b = 2.07, g_{bc}^a = 2.09$. The set of the anisotropic parameters $J'_c \sim -0.085 J$, $J'_b \sim 9 \times 10^{-4} J$

and $J'_a = 0$ well reproduces experimental data for the all directions $H \parallel a, b, c$. These estimates are somewhat different from those in ref. \[^17\]. In any case, the observed

small anisotropy in the $ab$-plane is consistent with the treatment in ref. \[^13\].

Overall, the observed temperature dependence is well

reproduced by our theory down close to Néel temperature $T_N \sim 2.3\text{ K}$, where the interchain interactions should be important also for ESR. Discrepancies are however found in the high temperature regime ($>200\text{K}$) for all the three directions of $H$ in ref. \[^14\], and in the low temperature regime ($<50\text{K}$) for $H \parallel c$ in ref. \[^14\]. The former could be due to the low signal-to-noise ratio at high temperatures. The latter data may be also questionable for the absence of the anomaly (presumably related to the higher dimensional effects) below $10\text{K}$, which are observed in all the other data set.

The estimated values of the exchange anisotropy, especially $J'_c/J \sim -0.15$ for the data from ref. \[^13\], seems too large compared to the typical value of a percent for a Cu ion. This could be due to a possible overestimation of the $g$-shift in the analysis in ref. \[^13\] to extract the direction-dependent effective $g$-factor from the direction-averaged data on the powder sample.

In any case, the temperature dependence of the $g$-shift of LiCuVO$_4$ is better accounted by the present theory than by the classical one \[^5\], especially at low temperatures. We hope that the present study stimulates further experimental studies on the $S = 1/2$ antiferromagnetic chain for more precise comparisons with the theory.

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\[^17\] The value of $J$ is twice of $22\text{K}$ in ref. \[^13\] \[^15\] due to the different definition of $J$.\[^7\]