Magnetotropic Response in Ruthenium Chloride

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We consider the exchange couplings present in an effective Hamiltonian of α-RuCl₃, known as the K-Γ model. This material has a honeycomb lattice, and is expected to be a representative of the Kitaev materials (which can realize the 2d Kitaev model). However, the behaviour of RuCl₃ shows that the exchange interactions of the material are not purely Kitaev-like, especially because it has an antiferromagnetic ordering at low temperatures and under low strengths of an externally applied magnetic field. Fitting the data obtained from the measurements of the magnetotropic coefficient (the thermodynamic coefficient associated with magnetic anisotropy), reported in Nature Physics 17, 240–244 (2021), we estimate the values of the exchange couplings of the effective Hamiltonian. The fits indicate that the Kitaev couplings are subdominant to the other exchange couplings.

Keywords: α-RuCl₃; magnetotropic coefficient; K-Γ model

I. INTRODUCTION

Spin-orbit coupling (SOC) assisted (spin $j = 1/2$) Mott insulators, exhibiting bond-directional exchange interactions, are expected to exhibit unconventional quantum magnetic phases like spin liquids [1, 2], predicted by the two-dimensional (2d) Kitaev model [3] on honeycomb lattice. These putative quantum spin liquids are dubbed as “Kitaev spin liquids” (KSLs) [4–8], and the materials expected to show such behaviour are called Kitaev materials. Compounds like honeycomb iridates and α-RuCl₃ have been identified as candidate Kitaev materials. The hallmark feature of a Kitaev material is that the Kitaev coupling is the dominant exchange coupling. However, the behaviour of RuCl₃ shows that the exchange interactions of the material are not purely Kitaev-like. In this paper, we will address the unresolved question regarding what the possible exchange couplings in α-RuCl₃ could be – for example, what the dominant terms in the effective spin Hamiltonian are, and whether we can estimate the values of these coupling constants.

At low energies, experiments [12–14] show signatures consistent with a zig-zag antiferromagnet (AFM) background (also consistent with ab initio calculations [9, 15, 16]), while indicating the existence of an unconventional quantum magnetic phase, which could be the much sought-after KSL induced by a finite magnetic field. Exact numerical diagonalization methods to investigate the data from dynamical spin structure factors, and that from heat capacity measurements [17, 18], found that off-diagonal interactions are dominant rather than Kitaev interactions [19]. On the other hand, other computational papers [7, 9, 10, 20] report that Kitaev terms are the dominant ones. We focus on the results from resonant torsion magnetometry experiments [21], which can measure the magnetotropic coefficient $k = \frac{\alpha^2 F}{\beta T}$ at temperature $T$. Here, $F = -\beta^{-1} \ln Z$ is the free energy, $\beta = \frac{1}{k_BT}$, and $\theta$ is the angle between the applied magnetic field $B$ and the $c$-axis of the crystal. Using a simple Hamiltonian with a dominant paramagnetic term, we will show that we can fit the data obtained from the measurements of the magnetotropic coefficient, and the fits correspond to the Kitaev terms being subdominant in the so-called K-Γ model.

II. MODEL

Due to the presence of on-site SOC, the effective magnetic field components along the spin projections are given by:

$$\tilde{B}_\alpha \equiv B_\alpha D_{\gamma \alpha}, \quad [D] = \mathcal{A} \mathbb{I}_{3\times3} + \begin{pmatrix} 0 & B & B \\ B & 0 & B \\ B & B & 0 \end{pmatrix},$$

(2.1)

where the form of $[D]$ has been fixed by the $C_3$ and $C_2$ rotation symmetries [22] of P3$_1$12, constraining it to have $A$ and $B$ as the only two independent components (see Appendix A). In the abc-coordinate system, $[D]$ is rotated to take the diagonal form, $\text{diag}\{g_a, g_a, g_c\}$, where the $g$-factors are given by:

$$\tilde{g}_a = \frac{k_B g_a}{\mu_B}, \quad \tilde{g}_c = \frac{k_B g_c}{\mu_B}, \quad g_a = A - B, \quad g_c = A + 2B,$$

(2.2)

such that $k_B = 1.38064852 \times 10^{-23} J/K$ and $\mu_B = 9.274 \times 10^{-24} J/T$. The SOC thus forces the leading order paramagnetic term in our model Hamiltonian to be $H_0 = -\sum_{\alpha=x,y,z} \tilde{B}_\alpha \sigma_\alpha^\alpha$, rather than $-\sum_{\alpha=x,y,z} B_\alpha \sigma_\alpha^\alpha$. We note that the Hamiltonian has the

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units of \( g \mu_B \mathbf{r} \cdot \mathbf{B} \) (\( \mathbf{r} \) is the dimensionless spin-1/2 vector operator), such that \( \frac{g \mu_B \mathbf{r} \cdot \mathbf{B}}{k_B T} \) is dimensionless (because we have factors like \( e^{-\beta H} \)). Hence, \( A \) and \( B \) have units of \( K/T \).

Following the arguments above, the physics of a honeycomb lattice, restricted to nearest-neighbor interactions, and subjected to an external magnetic field \( B \), can indeed explain the experimental data, to a high degree of precision.

FIG. 1. Plots of \( k \) versus \( \theta \) computed from our theoretical model, where the orange curve represents the one obtained with the best-fit parameters for the \( (T = 20 K, B = 30 T) \) data-set, whereas the dotted blue curve has been drawn using those same parameters, except that we have set \( D = 0 \). This clearly shows that we can never get an asymmetric spike around \( \theta = 0 \) without an asymmetric off-diagonal \( \Gamma \) term, which represents DM interactions.

\[
\mathcal{Z}(T) = \left[ 2 \cosh \left( \frac{\beta \tilde{B}}{2} \right) \right]^{2N_c} \left[ 1 + \beta N_c \sum_{\gamma, \alpha', \lambda'} J_{\alpha' \lambda'} \frac{\sinh \left( \frac{\beta \tilde{B}}{2} \right) \sinh \left( \beta \tilde{B} \lambda' \right)}{\cosh^2 \left( \frac{\beta \tilde{B}}{2} \right)} \right], \quad \text{where} \quad \tilde{B} = \sqrt{\sum_{\alpha} \tilde{B}_\alpha \tilde{B}_\alpha},
\]

where \( N_c \) is the number of unit cells (or, half the number of honeycomb lattice sites) in the system. It turns out that this simple model can indeed explain the experimental data, to a high degree of precision.
FIG. 2. The data-sets for \( k \) versus \( \theta \) (in radians) at \( T = 20 \, K \) for various values of the applied magnetic field strength \( B \) (in units of Tesla). We have represented the experimental data-points in blue, and the best-fit curves in orange.

| \( B = 20 \, T \) | Estimate | Standard Error | Confidence Interval |
|------------------|----------|----------------|---------------------|
| \( \kappa \)     | 54.4     | 2.37           | {52.1, 56.7}        |
| \( \Gamma \)     | 102      | 6.09           | {96.8, 108}         |
| \( D \)          | -9.60    | 0.629          | {-10.2, -8.98}      |
| \( g_a \)        | 4.00     | 0.137          | {3.87, 4.13}        |
| \( g_c \)        | 1.79     | 0.0984         | {1.70, 1.89}        |
| \( \zeta \)      | 2.00     | 0.0736         | {1.93, 2.07}        |
| \( \eta \)       | -9.38    | 0.150          | {-9.53, -9.23}      |

| \( B = 25 \, T \) | Estimate | Standard Error | Confidence Interval |
|------------------|----------|----------------|---------------------|
| \( \kappa \)     | 74.6     | 1.32           | {73.3, 75.9}        |
| \( \Gamma \)     | 133      | 8.80           | {125, 142}          |
| \( D \)          | -13.9    | 0.866          | {-14.7, -13.1}      |
| \( g_a \)        | 4.00     | 0.124          | {3.88, 4.12}        |
| \( g_c \)        | 1.52     | 0.0677         | {1.46, 1.59}        |
| \( \zeta \)      | 2.00     | 0.071          | {1.93, 2.07}        |
| \( \eta \)       | -24.4    | 0.281          | {-24.7, -24.2}      |

| \( B = 30 \, T \) | Estimate | Standard Error | Confidence Interval |
|------------------|----------|----------------|---------------------|
| \( \kappa \)     | 95.8     | 1.46           | {94.4, 97.3}        |
| \( \Gamma \)     | 152      | 9.46           | {143, 161}          |
| \( D \)          | -15.8    | 0.841          | {-16.6, -15.0}      |
| \( g_a \)        | 4.00     | 0.118          | {3.88, 4.11}        |
| \( g_c \)        | 1.26     | 0.0486         | {1.21, 1.30}        |
| \( \zeta \)      | 2.00     | 0.0687         | {1.93, 2.07}        |
| \( \eta \)       | -50.1    | 0.507          | {-50.6, -49.6}      |

| \( B = 34.5 \, T \) | Estimate | Standard Error | Confidence Interval |
|---------------------|----------|----------------|---------------------|
| \( \kappa \)       | 85.5     | 2.90           | {82.6, 88.3}        |
| \( \Gamma \)       | 156      | 28.7           | {128, 184}          |
| \( D \)            | -20.3    | 3.31           | {-23.5, -17.1}      |
| \( g_a \)          | 4.00     | 0.276          | {3.73, 4.27}        |
| \( g_c \)          | 1.20     | 0.122          | {1.08, 1.32}        |
| \( \zeta \)        | 2.00     | 0.145          | {1.86, 2.14}        |
| \( \eta \)         | -88.8    | 1.42           | {-90.2, -87.4}      |

TABLE I. The table shows the fitting of parameters at 67% confidence level, for the \( k \) versus \( \theta \) data-set. Here, \( B \) and \{\( \kappa, \Gamma, D \)\} are in units of \( T \), \{\( g_a, g_c \)\} are in units of \( K/T \), \( \zeta \) is dimensionless, and \( \eta \) has the same unit as \( k \).

III. FITTING THE DATA

According to some papers in the literature [9, 24], the point-group symmetry of the Ru-Ru links is \( C_{2h} \) in a \( C/2m \) unit cell, and hence the antisymmetric Dzyaloshinskii-Moriya (DM) exchange is zero. Because spin is an axial vector itself, the non-zero antisymmetric part of \( J_{\alpha\beta}^\gamma \) is equivalent to \( P \cdot (S \times S) \) term where \( P \) is a polar vector. So in order to have a DM term in exchange, the chemical environment of the Ru-Ru bond must allow for a polar vector. In the undistorted honeycomb lattice, such a polar vector is prohibited by symmetry. It is non-zero for next-nearest neighbor exchange links (even in the undistorted case) [25] or if Cl...
FIG. 3. We have plotted three curves corresponding to (1) leading order expression $k^{(0)}$; (2) first order correction $k^{(1)}$; and (3) $k^{(0)} + k^{(1)}$, as functions of $\theta$, which have been computed from our theoretical model, using the best-fit parameters for the ($T = 20 \text{ K}$, $B = 30 \text{ T}$) data-set. These three curves are shown in dashed yellow, dotted blue, and orange, respectively.

FIG. 4. The data-sets for $k$ versus $B$ (in units of Tesla) at $\theta = \pi/2$ for temperatures ranging from $T = 30 \text{ K}$ to $T = 150 \text{ K}$ at intervals of $10 \text{ K}$. The topmost curve represents the $30 \text{ K}$ data, whereas the lowermost curve represents the $150 \text{ K}$ data. We have represented the experimental data-points in blue, and the best-fit curves in orange.

The expressions for $F$ and $k$ depend on the polar angle $\theta$, but not on the azimuthal angle $\phi$. We fit the data-sets for four different values of the applied magnetic field strength $B$, using “NonlinearModelFit” of Mathematica. The data-sets for $B \leq 15 \text{ T}$ are not considered as they are either close to or within the AFM phase. Since the scaling and absolute shift of each data-set are uncertain, we include two more parameters, namely, “$\zeta$” and “$\eta$” corresponding to the unknown scale and shift. The experimental data and the fitted functions are shown in Fig. 2. The confidence intervals for all the parameters at 67% confidence level are shown in Table I.

We also fit the $k$ versus $B$ data available for $\theta = \pi/2$. One can check that the correction terms from $J^{\gamma}_{\alpha \beta}$ hardly affect the regions around $\theta = \pi/2$ (see Fig. 3). They have the most visible impact only around the $\theta = 0$ and $\theta = \pi$ regions. Hence, the fitting process keeping the first order correction makes the parameters indeterminate. However, if we fit only with the zeroth order expression, we get excellent values for $g_a$ and $g_c$. We also need to include a parameter “$\eta$” to account for the uncertainty in the absolute shift of the data-set for each temperature value. These fits are shown in Fig. 4. The data-sets for temperatures $T \leq 20 \text{ K}$ are not considered as each of them has a considerable region within the AFM phase in the low $B$ ranges, which cannot be fitted by the functional forms meant for the paramagnetic phase. The confidence intervals for $g_a$, $g_c$, and $\eta$, at 67% confidence level, are shown in Table II.
| $T = 30 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.43 | 0.00172 | {2.43, 2.44} |
| $g_ε$ | 1.20 | 0.00148 | {1.2, 1.20} |
| $η$ | 0.000131 | 0.0158 | {-0.0152, 0.0155} |

| $T = 50 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.42 | 0.000581 | {2.42, 2.42} |
| $g_ε$ | 1.23 | 0.00600 | {1.23, 1.23} |
| $η$ | 0.00822 | 0.0473 | {0.00362, 0.0128} |

| $T = 70 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.28 | 0.00920 | {2.28, 2.28} |
| $g_ε$ | 1.20 | 0.0113 | {1.20, 1.20} |
| $η$ | 0.00923 | 0.0490 | {0.00446, 0.0140} |

| $T = 90 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.12 | 0.00235 | {2.12, 2.12} |
| $g_ε$ | 1.20 | 0.00316 | {1.20, 1.20} |
| $η$ | -0.0124 | 0.00691 | {0.0191, -0.00565} |

| $T = 110 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 1.94 | 0.00531 | {1.94, 1.95} |
| $g_ε$ | 1.20 | 0.00732 | {1.19, 1.201} |
| $η$ | -0.00637 | 0.0078 | {-0.014, 0.00123} |

| $T = 150 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 1.76 | 0.0953 | {1.66, 1.85} |
| $g_ε$ | 1.287 | 0.122 | {1.17, 1.41} |
| $η$ | -0.00276 | 0.0385 | {-0.0403, 0.0347} |

| $T = 40 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.46 | 0.000785 | {2.46, 2.46} |
| $g_ε$ | 1.24 | 0.000738 | {1.24, 1.24} |
| $η$ | 0.000267 | 0.0070 | {-0.00655, 0.00709} |

| $T = 60 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.34 | 0.000456 | {2.34, 2.34} |
| $g_ε$ | 1.20 | 0.00518 | {1.20, 1.20} |
| $η$ | 0.00592 | 0.00310 | {0.00290, 0.00894} |

| $T = 70 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.20 | 0.00158 | {2.2, 2.2} |
| $g_ε$ | 1.20 | 0.00204 | {1.20, 1.20} |
| $η$ | 0.0452 | 0.00637 | {0.039, 0.0514} |

| $T = 80 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 2.03 | 0.00351 | {2.03, 2.03} |
| $g_ε$ | 1.20 | 0.00481 | {1.20, 1.20} |
| $η$ | 0.043 | 0.00740 | {0.0358, 0.0503} |

| $T = 90 \, K$ | Estimate | Standard Error | Confidence Interval |
|---|---|---|---|
| $g_α$ | 1.79 | 0.0111 | {1.78, 1.80} |
| $g_ε$ | 1.20 | 0.0151 | {1.18, 1.21} |
| $η$ | -0.0081 | 0.00815 | {-0.016, -0.000166} |

TABLE II. The table shows the fitting of parameters at 67% confidence level, for the $k$ versus $B$ data-set. Here, temperature $T$ is in units of Kelvin ($K$), $\{g_α, g_ε\}$ are in units of $K/T$, and $η$ has the same unit as $k$.

IV. SUMMARY AND OUTLOOK

Let us discuss some other possibilities which might be responsible for causing the asymmetry in the spike around $θ = 0$ in the $k$ versus $θ$ data. Firstly, in the experimental set-ups, the path along which the sample is rotated in the external magnetic field to change $θ$, may deviate from a great circle, leading to an uncertainty of up to 10°. However, incorporating these deviations, the theoretical curves do not show the desired asymmetry [26]. Secondly, the K-$Γ$ Hamiltonian (even without DM, distortion, misalignment of rotation etc.) lacks mirror reflection symmetry. Therefore, magnetotropenic coefficients (or free energy) are different for applied magnetic fields, $B$ and $B'$, that are related by a mirror reflection in honeycomb plane. Such asymmetry is artificially removed in low-order perturbation theory. This is directly analogous to accidental symmetries of the standard model (such as separate conservation of baryon and lepton number) that only exist in the lowest order of expansion in inverse GUT scale. It is a general phenomenon – low orders in perturbation theory tend to accidentally “restore” some of the symmetries of the Hamiltonian In the Kitaev model, the lowest order perturbation expansion in magnetic field [3] is symmetric (with respect to mirror- $ab$-plane) – one needs to go to higher orders in $B$ to see the asymmetry of the Hamiltonian. The same might be true for the thermodynamic perturbative expansion. By going to higher orders (second, or maybe third order), the asymmetric character of the Hamiltonian may eventually show up. However, such higher order computations are beyond the scope of this paper.

Our best-fit parameters show that the Kitaev terms are subdominant to the $Γ$ (and $D$) terms. In fact, the large $Γ$ value contrasts with the expectation so far [7, 9, 10, 20] that $α$-RuCl$_3$ is a “Kitaev model material”. It has also been predicted [9, 20, 27] in those models (including a small Heisenberg term) that the ratio $g_ε/g_α \approx 0.4 – 0.5$. Our results (see Fig. I) are close to these results, although we should remember that our model differs from theirs.

V. ACKNOWLEDGMENTS

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We choose a coordinate system such that the plane of the honeycomb lattice is described by three in-plane vectors \( \mathbf{r}_1 = (0, 1, -1) \), \( \mathbf{r}_2 = (-1, 1, 0) \), \( \mathbf{r}_3 = (-1, 0, 1) \), as they lie on the plane formed by cutting the three points: \( (1, 0, 0), (0, 1, 0) \) and \( (0, 0, 1) \). Then the perpendicular vector is \( \mathbf{r}_\perp = (1, 1, 1)/\sqrt{3} \) and we choose the in-plane direction as \( \mathbf{r}_2/\sqrt{2} \), giving \( \mathbf{B} = \frac{\cos \theta (1, 1, 1)}{\sqrt{2}} + \sin \theta (-1, 1, 0) \), with the magnetic field making an angle \( \theta \) with the \( c \)-axis. Let us also define the \( a \)-axis along the line joining \( (1, 1, 1)/3 \) and \( (1, 0, 0) \), such that the projection of \( \mathbf{B} \) on the \( ab \)-plane makes an angle \( \phi \) with the \( a \)-axis.

Given a unit vector \( \mathbf{u} \), the matrix for a rotation by an angle of \( \phi \) about an axis in the direction of \( \mathbf{u} \) is:

\[
R(\mathbf{u}, \phi) = \begin{pmatrix}
\cos \phi + u_x^2 (1 - \cos \phi) & u_x u_y (1 - \cos \phi) - u_z \sin \phi & u_x u_z (1 - \cos \phi) + u_y \sin \phi \\
u_y u_x (1 - \cos \phi) + u_z \sin \phi & \cos \phi + u_y^2 (1 - \cos \phi) & u_y u_z (1 - \cos \phi) - u_x \sin \phi \\
u_z u_x (1 - \cos \phi) - u_y \sin \phi & u_z u_y (1 - \cos \phi) + u_x \sin \phi & \cos \phi + u_z^2 (1 - \cos \phi)
\end{pmatrix} .
\] (A1)

Now the crystal symmetry allows invariance under a \( C_3 \) rotation about \( \mathbf{r}_\perp \), which corresponds to invariance under the rotation matrix:

\[
R(\mathbf{r}_\perp, 2 \pi/3) = \begin{pmatrix}
0 & 0 & 1 \\
1 & 0 & 0 \\
0 & 1 & 0
\end{pmatrix} .
\] (A2)

For \( C_2 \) rotation about \( \mathbf{r}_1 \), we have:

\[
R\left(\frac{\mathbf{r}_1}{\sqrt{2}}, \pi\right) = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 0 & -1 \\
0 & 1 & 0
\end{pmatrix} .
\] (A3)

Due to on-site spin-orbit coupling, the leading order paramagnetic term in our model is given by \( H = - \sum_{\alpha=x,y,z} \tilde{B}_\alpha \sigma^\alpha_3 \), rather than \( - \sum_{\alpha=x,y,z} B_\alpha \sigma^\alpha_3 \), where \( \tilde{B}_\alpha \equiv B_\gamma D_{\gamma \alpha} \). We still have the \( C_3 \) and \( C_2 \) rotation symmetries of P3_1 12 [22] to be satisfied, which implies that:

\[
[B]^T [D] [\sigma] = (R[B])^T [D] R[\sigma] \Rightarrow D = R^T [D] R,
\] (A4)

where \( R \) has been defined in Eq. \((A2)\). Then, \( R(\mathbf{r}_\perp, 2 \pi/3) \) and \( R\left(\frac{\mathbf{r}_1}{\sqrt{2}}, \pi\right) \) restrict \( [D] \) to have only two independent components, namely \( A \) and \( B \), such that

\[
[D] = A \mathbb{1}_{3\times3} + \begin{pmatrix}
0 & B & B \\
B & 0 & B \\
B & B & 0
\end{pmatrix} .
\] (A5)

Appendix B: Thermodynamic expansion of the K-\( \Gamma \) model in the large magnetic field limit

We perform a thermodynamic expansion of the K-\( \Gamma \) model in the large magnetic field limit, following the methods describe in Ref. 23, which are applicable when we are interested in the thermodynamic properties at finite temperature. We review this perturbation expansion when the Hamiltonian can be written as \( H = H_0 + \lambda V \), where \( H_0 \) is the leading order part for large \( B \), and \( \lambda \) is the perturbative expansion parameter, with \( V \) being the subleading part.

We are interested in the thermodynamic properties at finite temperature. Thus we start with the canonical partition function:

\[
Z(T) = \text{Tr} \left[ e^{-\beta H} \right] = \text{Tr} \left[ e^{-\beta (H_0 + \lambda V)} \right],
\] (B1)

and seek to expand its logarithm in powers of \( \lambda \). Since \( H_0 \) and \( V \) do not commute for the K-\( \Gamma \) model, we use the approach employed for interaction picture time evolution. We define the function \( f(\beta) \) by:

\[
e^{-\beta (H_0 + \lambda V)} = e^{-\beta H_0} f(\beta) \Rightarrow \frac{df(\beta)}{d\beta} = -\lambda e^{\beta H_0} V e^{-\beta H_0} f(\beta) .
\] (B2)

 Casting this in the form of the integral equation, we get:

\[
f(\beta) = 1 - \lambda \int_0^\beta d\tau \tilde{V}(\tau) f(\tau) , \quad \tilde{V}(\tau) = \lambda e^{\tau H_0} \sqrt{\frac{1}{V}} e^{-\tau H_0} f(\beta) .
\] (B3)
which we solve by iteration:

$$f(\beta) = 1 + \sum_{n=1}^{\infty} (-\lambda)^n \int_{0}^{\beta} d\tau_1 \int_{0}^{\tau_1} d\tau_2 \cdots \int_{0}^{\tau_{n-1}} d\tau_n \tilde{V}(\tau_1) \tilde{V}(\tau_2) \cdots \tilde{V}(\tau_n).$$  

(B4)

This gives us the partition function as:

$$\mathcal{Z}(T) = \mathcal{Z}_0 \left[ 1 + \sum_{n=1}^{\infty} (-\lambda)^n \int_{0}^{\beta} d\tau_1 \int_{0}^{\tau_1} d\tau_2 \cdots \int_{0}^{\tau_{n-1}} d\tau_n \langle \tilde{V}(\tau_1) \tilde{V}(\tau_2) \cdots \tilde{V}(\tau_n) \rangle_0 \right],$$  

(B5)

where $\langle \cdots \rangle_0$ denotes the unperturbed expectation value:

$$\langle A \rangle_0 = \frac{\text{Tr} [e^{-\beta H_0} A]}{\text{Tr} [e^{-\beta H_0}]}$$  

(B6)

for any operator $A$. The leading order term is given by:

$$\langle \tilde{V}(\tau) \rangle_0 = \frac{\text{Tr} [e^{-\beta H_0} e^\tau H_0 V e^{-\tau H_0}]}{\text{Tr} [e^{-\beta H_0}]} = \frac{\text{Tr} [e^{-\beta H_0} V]}{\text{Tr} [e^{-\beta H_0}]},$$  

(B7)

which is in fact independent of $\tau$.

Let us compute the leading term in the partition function for the Hamiltonian of the main text, such that:

$$H_0 = - \sum_{\alpha = \{x,y,z\}} \tilde{B}_\alpha \sigma^\alpha_j, \quad V = \sum_{\gamma, \langle jk \rangle_{\gamma^{-}\text{ink}}} \sum_{\lambda} J^\gamma_{\alpha \beta} \sigma^\alpha_j \sigma^\beta_k.$$  

(B8)

Hence, we get:

$$\langle \tilde{V}(\tau) \rangle_0 = \frac{\sum_{\gamma,\alpha,\lambda} \sum_{\langle jk \rangle_{\gamma^{-}\text{ink}}} J^\gamma_{\alpha \lambda} \sinh \left( \beta \tilde{B}_\alpha \right) \sinh \left( \beta \tilde{B}_\lambda \right)}{\cosh^2 \left( \beta \tilde{B} \right)} = \frac{N_c \sum_{\gamma,\alpha,\lambda} J^\gamma_{\alpha \lambda} \sinh \left( \beta \tilde{B}_\alpha \right) \sinh \left( \beta \tilde{B}_\lambda \right)}{\cosh^2 \left( \beta \tilde{B} \right)},$$  

(B9)

where $\tilde{B} = \sqrt{\sum_\alpha \tilde{B}_\alpha \tilde{B}_\alpha}$, and $N_c$ is the number of unit cells in the system. Finally, this gives us the partition function, corrected to leading order, as:

$$\mathcal{Z}(T) = \left[ 2 \cosh \left( \beta \tilde{B} \right) \right]^{2N_c} \left[ 1 + \beta N_c \sum_{\gamma,\alpha,\lambda} J^\gamma_{\alpha \lambda} \sinh \left( \beta \tilde{B}_\alpha \right) \sinh \left( \beta \tilde{B}_\lambda \right) \right].$$  

(B10)

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