Erratum: Computation of the Correlated Metal-Insulator Transition in Vanadium Dioxide from First Principles [Phys. Rev. Lett. 114, 176401 (2015)]

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(Received 19 December 2017; published 31 January 2018)

DOI: [10.1103/PhysRevLett.120.059901](https://doi.org/10.1103/PhysRevLett.120.059901)

We predicted that the insulating state in VO₂ would have a singlet-triplet excitation around 123(6) meV. Recently, inelastic x-ray scattering measurements [1] found this excitation at 460 meV. It has been noted that this result is far from the quantum Monte Carlo result we obtained [1,2]. On reanalysis of our original computational data, we noticed two errors that bring the results in closer alignment. The first error was due to a confusion of formula units and crystallographic units, and the second has to do with the interpretation of the calculation. The corrected value of the singlet-triplet gap from our quantum Monte Carlo calculation is 440(24) meV, which agrees with the experimental result within statistical error.

We computed the frozen spin states of the dimers, $|\uparrow\uparrow\rangle$ and $|\uparrow\downarrow\rangle$. For a dimer Heisenberg model,

$$H = JS_1 \cdot S_2 = \frac{1}{2}J[(S_1 + S_2)^2 - S_1^2 - S_2^2] = \frac{1}{2}J[s(s+1) - 3/2]. \quad (1)$$

For the two frozen spin states,

$$E(\uparrow\uparrow) = \langle\uparrow\uparrow|JS_1 \cdot S_2|\uparrow\uparrow\rangle = J/4 \quad (2)$$

and

$$E(\uparrow\downarrow) = \langle\uparrow\downarrow|JS_1 \cdot S_2|\uparrow\downarrow\rangle = -J/4. \quad (3)$$

The energy difference between these two states is thus $J/2$. The singlet eigenstate $\sqrt{1/2}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$ (with $s = 0$) has energy $-3J/4$ while the triplet eigenstate $|\uparrow\uparrow\rangle$ (with $s = 1$) has energy $J/4$, so the singlet-triplet excitation energy is J .

We computed using quantum Monte Carlo calculations the following difference of energy expectation values for VO₂ in the insulating state:

$$E(\uparrow\uparrow) - E(\uparrow\downarrow) = 123(6) \text{ meV/VO}_2. \quad (4)$$

The first error is that we should have computed energy per dimer, which is twice as large. The corrected equation for a dimer is thus

$$E(\uparrow\uparrow) - E(\uparrow\downarrow) = 246(12) \text{ meV/dimer} = J/2. \quad (5)$$

Our second error was setting $E(\uparrow\uparrow) - E(\uparrow\downarrow)$ as the singlet-triplet gap, which incorrectly ignored spin fluctuations as noted in the previous paragraph. Therefore, the singlet-triplet excitation is $J = 492(24)$ meV, within two statistical error bars of the experimental result. This realization was made possible by work we have done regarding effective model fitting [3,4]. We view this as a strong motivation to have a rigorous theory of effective models as we tried to lay out in those papers.

The above estimation of J ignores the weak interdimer coupling. One can include interdimer couplings using our calculations as well. In that case, the spin interaction is

$$\mathcal{H} = \sum_i J_{\text{intra}} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J_{\text{inter}} \mathbf{S}_{i+1} \cdot \mathbf{S}_{i+2} + E_0, \quad (6)$$

where $S_i = \frac{1}{2}\sigma_i$ and the σ_i 's are Pauli matrices. In our quantum Monte Carlo simulation, we calculated the energy of three frozen orders, the ferromagnetic order ($\uparrow\uparrow\uparrow\uparrow\dots$), antiferromagnetic order ($\uparrow\downarrow\uparrow\downarrow\dots$), and intra-antiferromagnetic order ($\uparrow\downarrow\downarrow\uparrow\dots$),

$$E_{\text{AFM}} = -\frac{N}{8}(J_{\text{intra}} + J_{\text{inter}}) + E_0, \quad (7a)$$

$$E_{\text{FM}} = \frac{N}{8}(J_{\text{intra}} + J_{\text{inter}}) + E_0, \quad (7b)$$

$$E_{\text{intraAFM}} = -\frac{N}{8}(J_{\text{intra}} - J_{\text{inter}}) + E_0, \quad (7c)$$

where N is the number of VO_2 formula units in the system. From Eq. (7) we obtain $J_{\text{intra}} = 4(E_{\text{FM}} - E_{\text{intraAFM}})/N = 440(24)$ meV, and $J_{\text{inter}} = 4(E_{\text{intraAFM}} - E_{\text{AFM}})/N = 52(24)$ meV [5]. The singlet-triplet excitation energy J_{intra} is 440(24) meV. This is slightly closer to the experimental value, but is a relatively small correction to the above two-site only model considering the statistical uncertainties.

In this case, the quantum Monte Carlo calculations helped to make it clear that indeed there should be a singlet-triplet excitation, and we hope that the experiments were partially motivated by the work to search for it. As a way of understanding the ground state of VO_2 , we view this as a resounding success. The quantum Monte Carlo results themselves were extremely accurate; it was our interpretation of the computational results that resulted in an incorrect quantitative prediction.

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- [5] Based on our quantum Monte Carlo results, $(E_{\text{FM}} - E_{\text{AFM}})/N = 123(6)$ meV, $(E_{\text{intraAFM}} - E_{\text{AFM}})/N = 13(6)$ meV.