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Revisiting the optical band gaps of Co_3O_4 using molecular methods

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In recent years, the antiferromagnetic material Co_3O_4 has been extensively studied for its experimentally observed optical band gaps [1–3]. Previous computational studies [4,5] of these properties have mainly relied on periodic approaches with DFT or Green function techniques. In this work, we present an additional novel perspective on the optical band gaps of Co_3O_4 by using molecular methods together with an electrostatic embedding approach [6,7].
Our protocol combines TD-DFT and multireference methods, such as SA-CASSCF/NEVPT2 [8] and MR-EOM-CC [9], yielding results in close agreement with experimental observations. Based on these results, a detailed analysis of the band gaps' origin is performed, linking the excited-state properties to the antiferromagnetic ground state of the material. Particular emphasis is placed on exploring the influence of both "ionic" and "neutral" antiferromagnetic states [10] inherent in the material, which can be specifically addressed using multireference methods. Our results highlight the significant impact of these states on the optical properties and their role in influencing the observed band gaps. This study contributes to a deeper understanding of the optical behavior of Co_3O_4 and emphasizes the importance of explicitly considering the antiferromagnetic ground states in comprehensive analyses of such materials.

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