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Trends in electron correlation effects on ^{17}O NMR chemical shifts in the alkaline earth oxides.[1] ERIC J. WALTER, DANIEL L. PECHKIS, HENRY KRAKAUER, College of William & Mary — A recent study found that calculated GGA chemical shift δ_{iso}(O) in CaO and other Ca oxides were in poor agreement with experiment. We have calculated δ_{iso}(O) in the rock salt series MgO through BaO, using a range of methods from HF and DFT to highly accurate CCSD calculations. The crystal environments were modeled with finite quantum clusters. GGA results for 25-atom $O_{19}X_6$ embedded clusters are found to i) reproduce previous GGA results with periodic boundary conditions for Mg and Ca[2]; ii) yield poor results for SrO as in CaO; iii) give good agreement with experiment for BaO. 7-atom OX_6 clusters were used to study trends with increasing levels of correlation. For MgO, correlated treatments result in only small changes compared to HF and DFT, as expected. Both CaO and SrO show large changes due to improved treatment of correlation, with the GGA-CCSD δ_{iso}(O) difference similar to the GGA-Expt difference in the larger clusters. CCSD OX_6 results for BaO were inconclusive, from competing errors due to relativistic and correlation effects. We discuss our results in terms of the increasing covalency in XO crystals with heavier cations.

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[2]Profeta et al. J. Am. Chem. Soc. **126**, 12628 (2004).

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