Assessing the Accuracy of Quantum Monte Carlo Pseudopotentials for CO_2 Capture in Metal Organic Frameworks

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Global warming has become a rising threat over the years as global emissions of carbon dioxide rise. The elevated levels of CO_2 and other greenhouse gasses trap heat in the earth's surface and lead to a rise in global temperatures, as well as increasing weather phenomena. One method of combatting this climate crisis, is finding materials to capture CO_2. A particularly promising material are Metal Organic Frameworks, or MOFs. These materials, a combination of metal centers and organic ligands can be fine tuned to selectively capture gasses, such as CO_2. However, given the vast array of MOFs possible, computational chemistry is necessary to selectively chose the appropriate MOF.

With the rise in technology, MOFs can be computationally modelled. For larger materials such as MOFs, Density Functional Theory, or DFT, has traditionally been used. However, DFT has been shown to lack accuracy when modelling materials with transition metals, such as MOFs. Diffusion Monte Carlo, DMC, has been shown to not have these same transition metal errors, and is being explored for its ability to model MOFs. However, both these methods require the use of approximations. One of these approximations is pseudopotentials. Electron-Electron interactions are nearly impossible to model for most systems, so pseudopotentials replace inner electrons, and simplify calculations. This research project focused on testing pseudopotentials newly developed for DMC use on MOFs. [1] The MOF used was M-MOF-74 (M = Mg, Zn, Fe, Co, Mn, Cu).

To accomplish these goals, GAMESS software was used to run DFT calculations on the MOF, the MOF with CO_2 and CO_2 alone. The binding energy was calculated using the formula:

$$\mathbf{BindingEnergy = E_{MOF+CO2} - E_{MOF} - E_{CO2}}$$

DFT calculations were run since DMC requires a starting wavefunction. The generated wavefunction was then used for DMC calculations. The DMC calculations were run using QMCPAK and involve a trial wavefunction generation, a trial wavefunction optimization, and then the actual DMC calculations. I ran these calculations using different basis sets, for Fe, Co, and Zn. The results are being processed by other group members, but for the cc.VDZ basis set, (pseudopotential) for Zn-MOF-74, they show that the DMC calculations gave a more accurate binding energy than the DFT calculations when compared to literature. No conclusions can be made about the accuracy of these pseudopotentials until further basis sets and metals are assessed.

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References:

1. https://pseudopotentiallibrary.org/