# Quantum Monte Carlo making progress with metal surfaces: CO adsorbed on Cu(100) and Pt(100)

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For periodic solids, Quantum Monte Carlo (QMC) simulations must overcome a restriction on the size of wave functions due to 'unflolding' the k-point grid in the First Brillouin Zone. This multiplies the content by the number of k-points and rapidly the wave functions get too large for supercalculator memory. It is necessary to use this hardware, and even with shared memory, in practice, the k-point grid is limited to about 2 2 2, which is generally too small to converge values of physical properties.

The phenomenon is known as finite size effect. It can be corrected by fitting to DFT calculations but is non negligible. It is particularly large for delocalised systems like metals.

In this work, it is shown that between single k-point wave functions and those with 4 k-points, a factor of at least 25 is gained in the finite size effect for Cu(100) and Pt(100). It is also shown that the effect is little influenced by the presence of adsorbed CO. This leads us to be optimistic for cancelation of the associated errors during adsorbtion and even heterogeneous catalysis.

Nevertheless, an ad hoc fitting to DFT work is also used.

Previous work, [1] gives a 3-body correlation ansatz applied to the copper catalyst.
Some of the present results are detailed in [2].

[1] P.E. Hoggan, *Int. J. Quantum Chem.* 113 (2013) 277 and

[2] P.E. Hoggan and A. Bouferguène, *Adv. Quantum Chem.* 67 (2014) accepted.