Change in electron and spin density upon electron transfer to haem *a*

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Haem *a* is the low-spin, bis-imidazol-ligated iron-porphyrin cofactor in many of the respiratory haem-copper oxidases, which catalyse most of the biological consumption of O_2. Its structure is related to many other haem groups, the typical redox cofactor of cytochromes. Haem *a*, like many other haems, functions in electron transfer, which involves continuous shuttling between its oxidised ("ferric") and reduced ("ferrous") states. Here we show by quantum-chemical calculations that the unit charge by which these two states differ is evenly distributed throughout the haem's porphyrin ring, the charge difference at the haem iron being very small despite the formal unit difference in oxidation state. In contrast, the unpaired spin density in the oxidised haem is found to be exclusively located at the haem iron in agreement with spectroscopic observations. Thus, while addition of an electron to the oxidised haem pairs the spin on the haem iron, there is in addition substantial pairwise electron delocalisation towards the haem's periphery on reduction.