

Using the IBM-SP as a Computational Catalysis Tool: What Does Hydrogen do in CeO₂?

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Parallelization and fast processors on **Eagle** quicken a key calculation from 38.9 days (projected on a local workstation) to just 5 hours 45 mins.

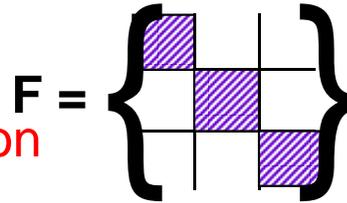
By some accounts, catalysis impacts $\geq 30\%$ of GDP in developed countries[1]. Catalysis impacts the production of fuel products, the synthesis of bulk and fine chemicals, and automotive emissions control. Automotive catalysis is a field where the demand for innovation is constant even in times of flat or declining sales, because it is driven by regulation[2]. Current emissions are at about 1 % of pre-regulatory levels, but ever-tightening regulations are anticipated well into the next decade[3].

Cerium oxide (ceria) is a critical and multi-functional component of automotive emissions catalysts[4]. One function of ceria is to act as an “oxygen storage” component. Ceria is capable of oxygen uptake during excursions of the air/fuel ratio into the net oxidizing regime, and oxygen release during excursions into the reducing regime, thus facilitating sustained CO and HC oxidation and simultaneous NO_x reduction, ie. *three way* catalysis (TWC). Cerium oxide is also known to extend the lifetime of the noble metal component of the catalyst, and to lower the effective activation barrier to CO oxidation, thus improving the catalyst performance at engine startup[4].

Many of the key properties of ceria that contribute to its success in automotive catalysis are thought to arise from the fact that cerium has two stable oxidation states, Ce⁺³ and Ce⁺⁴. As a consequence, cerium oxide may exist over a range of possible stoichiometries CeO_(2-x) [0 ≤ x ≤ 0.5]. The deviation of ceria from its ideal CeO₂ composition has been extensively studied by temperature programmed reduction with hydrogen[5]. These studies have given rise to an important controversy: During reduction with hydrogen, is there hydrogen uptake by ceria?

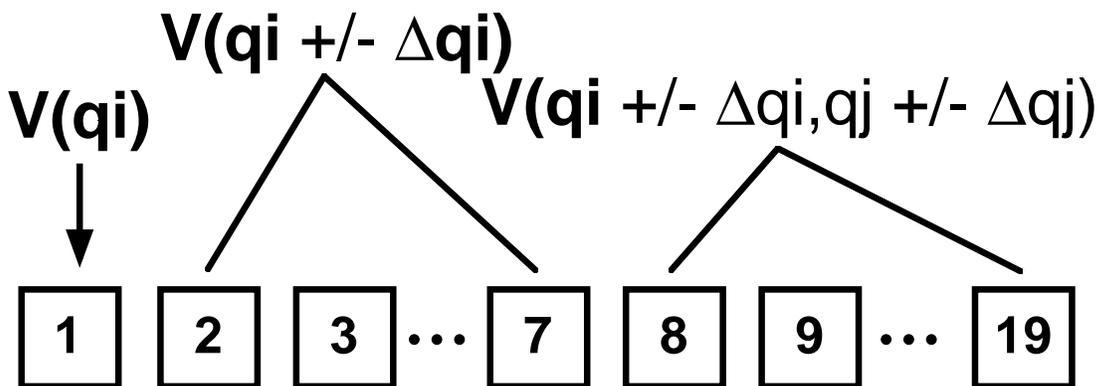
The presence of hydrogen in ceria has been probed by infrared absorption spectroscopy (IR), and characteristic bands have been identified, but a theoretical prediction of the hydrogen vibrational frequencies is needed to positively assign the bands. Unfortunately, the same property that makes ceria so useful in automotive catalysis, the fact that cerium has two stable oxidation states, also renders it a very challenging system to treat computationally. **With Eagle, the computational challenge of computing vibrational frequencies for hydrogen in ceria with accurate first-principles methods has been met.**

The elements of the force constant matrix \mathbf{F} are approximated by numerical second derivatives. The function evaluations are distributed across 19 processors.

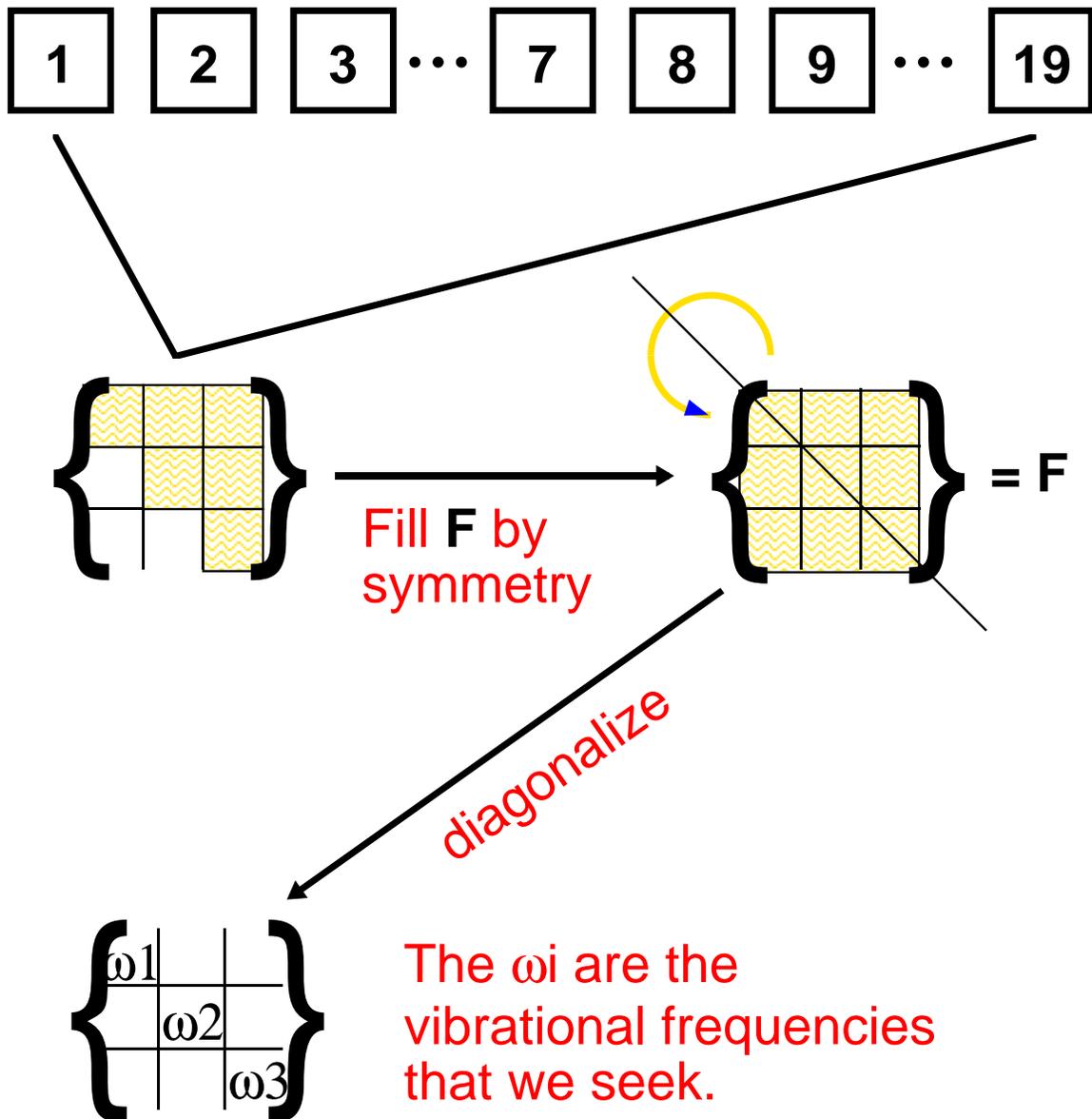


$$\blacksquare = \frac{\partial^2 V}{\partial q_i^2} \approx \frac{\{V(q_i + \Delta q_i) - 2V(q_i) + V(q_i - \Delta q_i)\}}{\{\Delta q_i\}^2}$$

$$\square = \frac{\partial^2 V}{\partial q_i \partial q_j} \approx \frac{\{V(q_i + \Delta q_i, q_j + \Delta q_j) - V(q_i + \Delta q_i, q_j - \Delta q_j) + V(q_i - \Delta q_i, q_j + \Delta q_j) - V(q_i - \Delta q_i, q_j - \Delta q_j)\}}{\{4\Delta q_i \Delta q_j\}}$$



The function evaluations from the 19 processors are combined to determine the **F** matrix elements.



Details and Acknowledgements

The parallel implementation of the vibrational analysis scheme was first tested on a simpler problem, hydrogen vibrations in hydrogen-doped alumina, which had been carried out successfully on a local workstation. The single-processor workstation took 44 hours of CPU time to complete the calculation, **Eagle** turned the problem around in 1 hour 50 mins. by the wall clock! The results were in excellent agreement with experiments[6], thus validating not only the methodology, but also the parallel implementation.

We projected the hydrogen-doped ceria calculation to take 38.9 days on the local workstation. Despite several attempts, we were never able to complete the calculation. **Eagle** turned the problem around in a stunning 5 hours 45 mins. While this result probably indicates that the original estimate was conservative, it clearly demonstrates that employing **Eagle** makes a unreasonably long calculation, reasonable.

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