

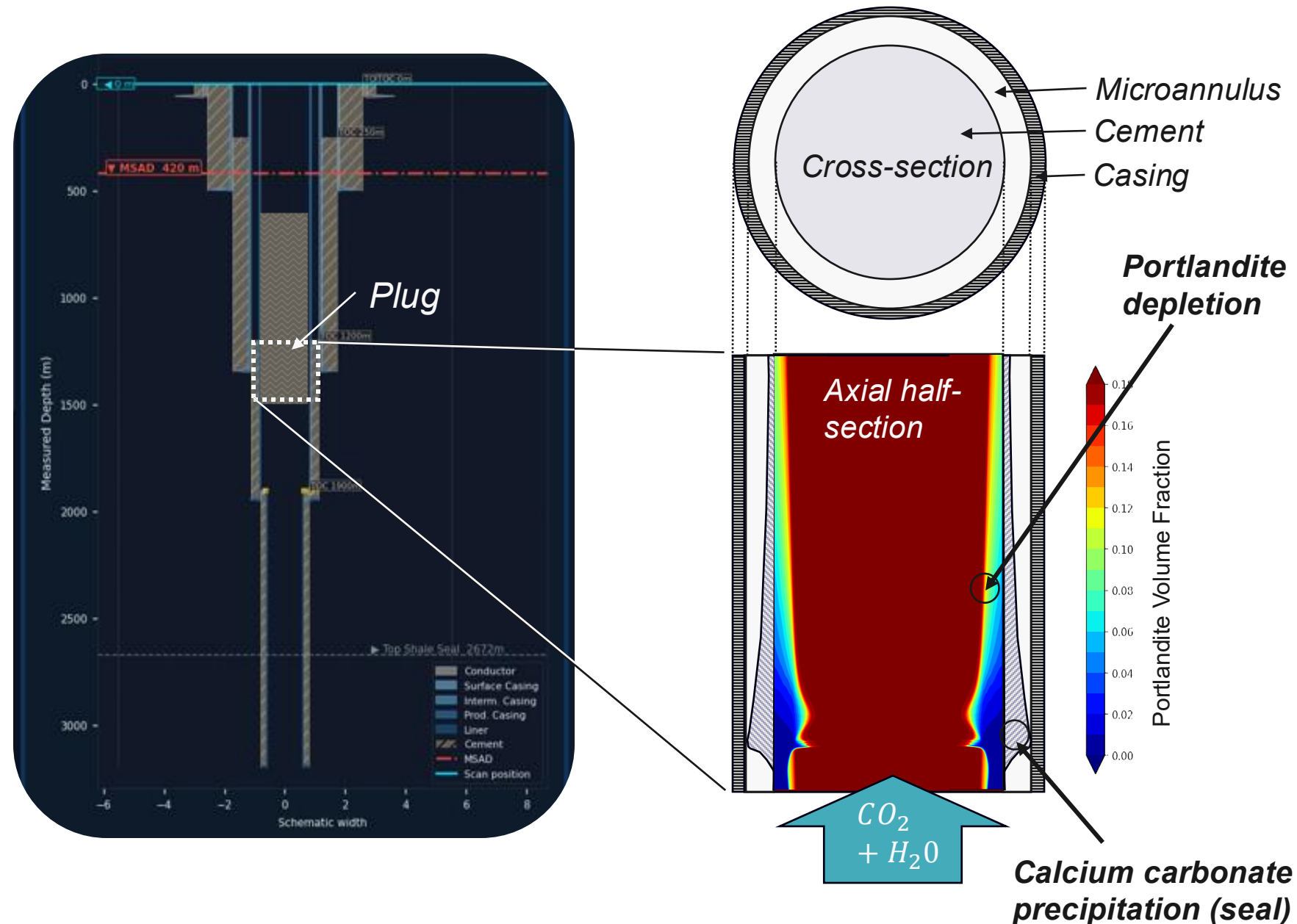
From the Beginning... Ab Initio Insights into Cement-CO₂ Reactions for CCS Wellbore Integrity (Printed Version)

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Cement Self Sealing

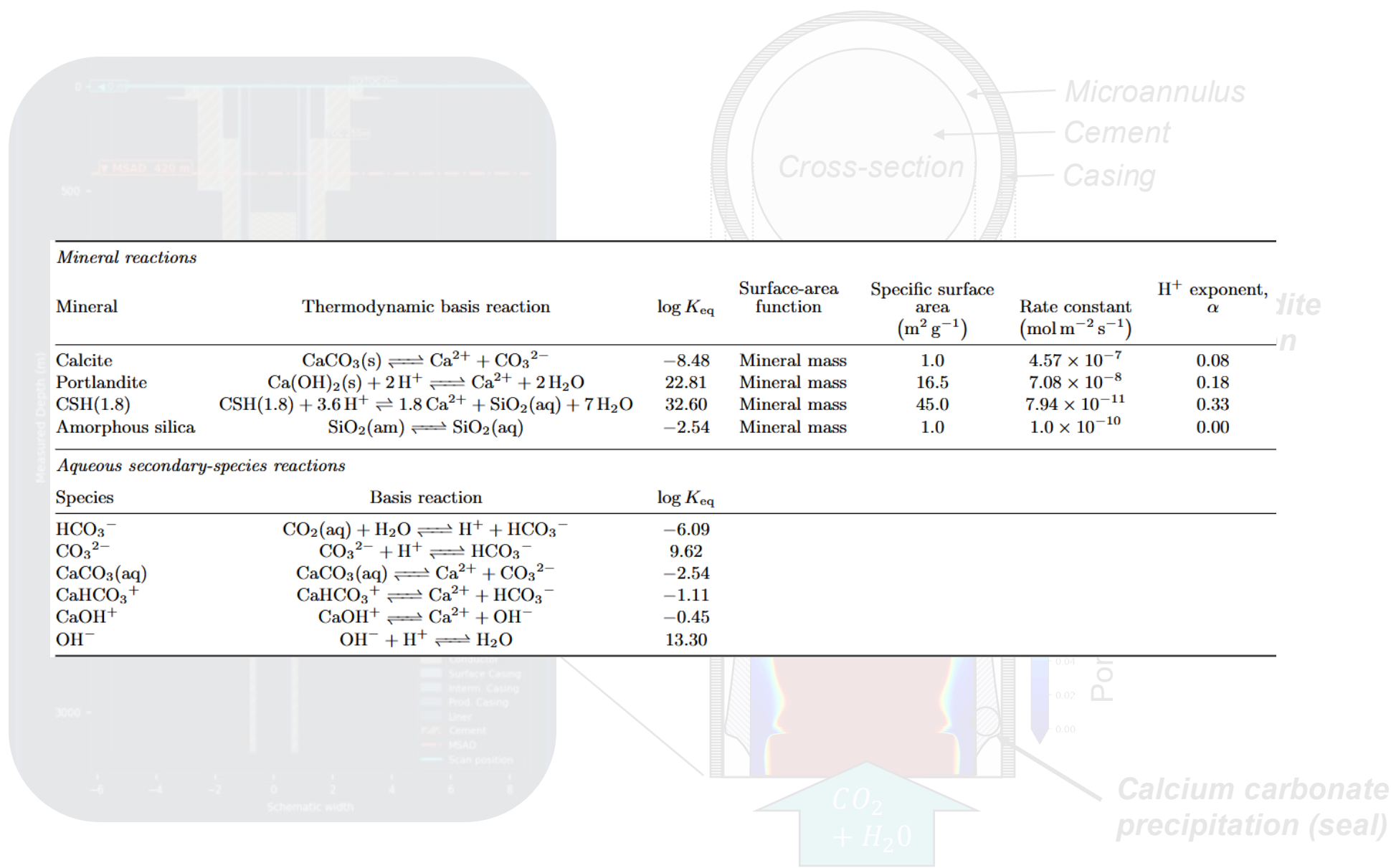


A key question is whether cement can "self-seal" following exposure to CO₂-rich fluids. On the far left, we show a full well-scale model of a legacy wellbore within a formation being considered for CO₂ storage. At this scale, we can identify potential leakage pathways and examine where CO₂ may come into contact with cement barriers, such as a cement plug containing a microannulus (as considered on the right).

We then "zoom in" to the metre scale, where reactive transport within the microannulus can be resolved in much greater detail.

First, portlandite is progressively depleted, releasing calcium into solution. Then, if under suitable conditions, this calcium precipitates as calcium carbonate within the microannulus. As calcium carbonate accumulates, the microannulus becomes increasingly restricted and can ultimately form a mineral "seal", preventing further upward migration of CO₂-rich fluid...

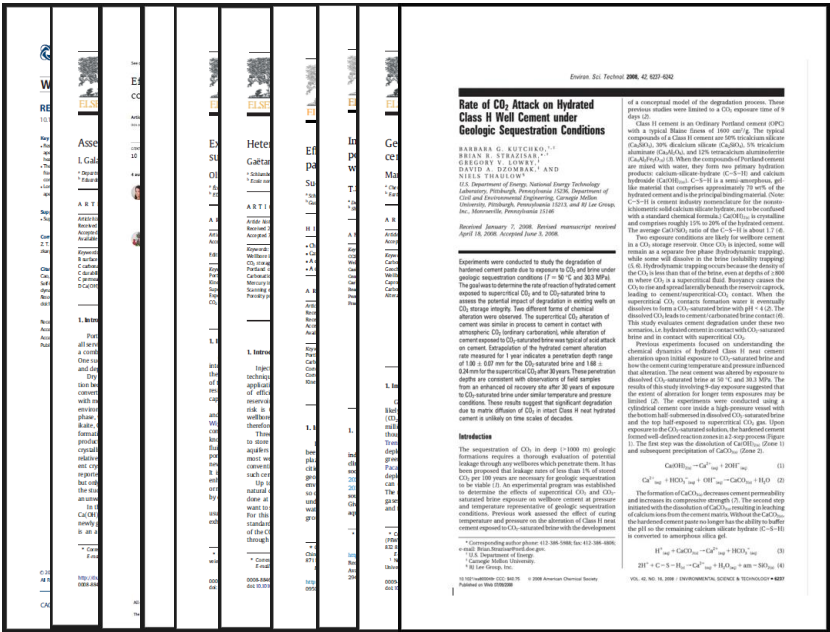
Cement Self Sealing



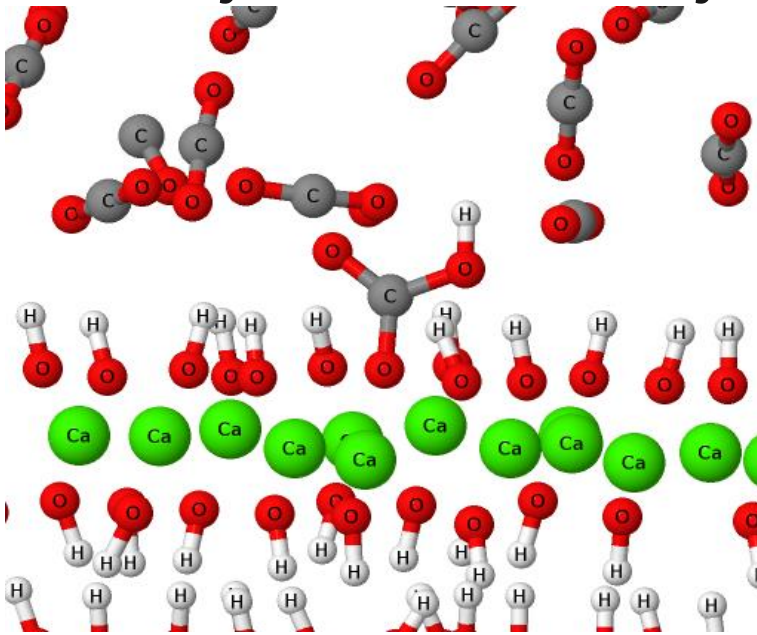
....however, these models are only as reliable as the parameters used to define them. Of particular importance to the self-sealing mechanism are the chosen kinetic and thermodynamic parameters, an example of which is shown here. These parameters strongly influence whether sealing will occur in our numerical models.

Cement Self Sealing

Experimental Observations



Density Functional Theory



Currently, these parameters are largely derived from experimental observations, with multiple studies used to establish a plausible range of values. Numerical models can then be further calibrated against experiments that resemble the system of interest.

This creates two challenges. First, no two experiments are identical: even studies examining the same process can differ substantially in materials, geometry, and operating conditions.

Second, experiments are necessarily limited in duration, typically lasting days to months rather than the thousands of years relevant to geological storage.

We are therefore using highly variable, short-term, experimental data to parameterise models expected to make very long-term predictions. Hence, our aim is to strengthen this experimental basis with an independent computational approach: Density Functional Theory, or DFT.

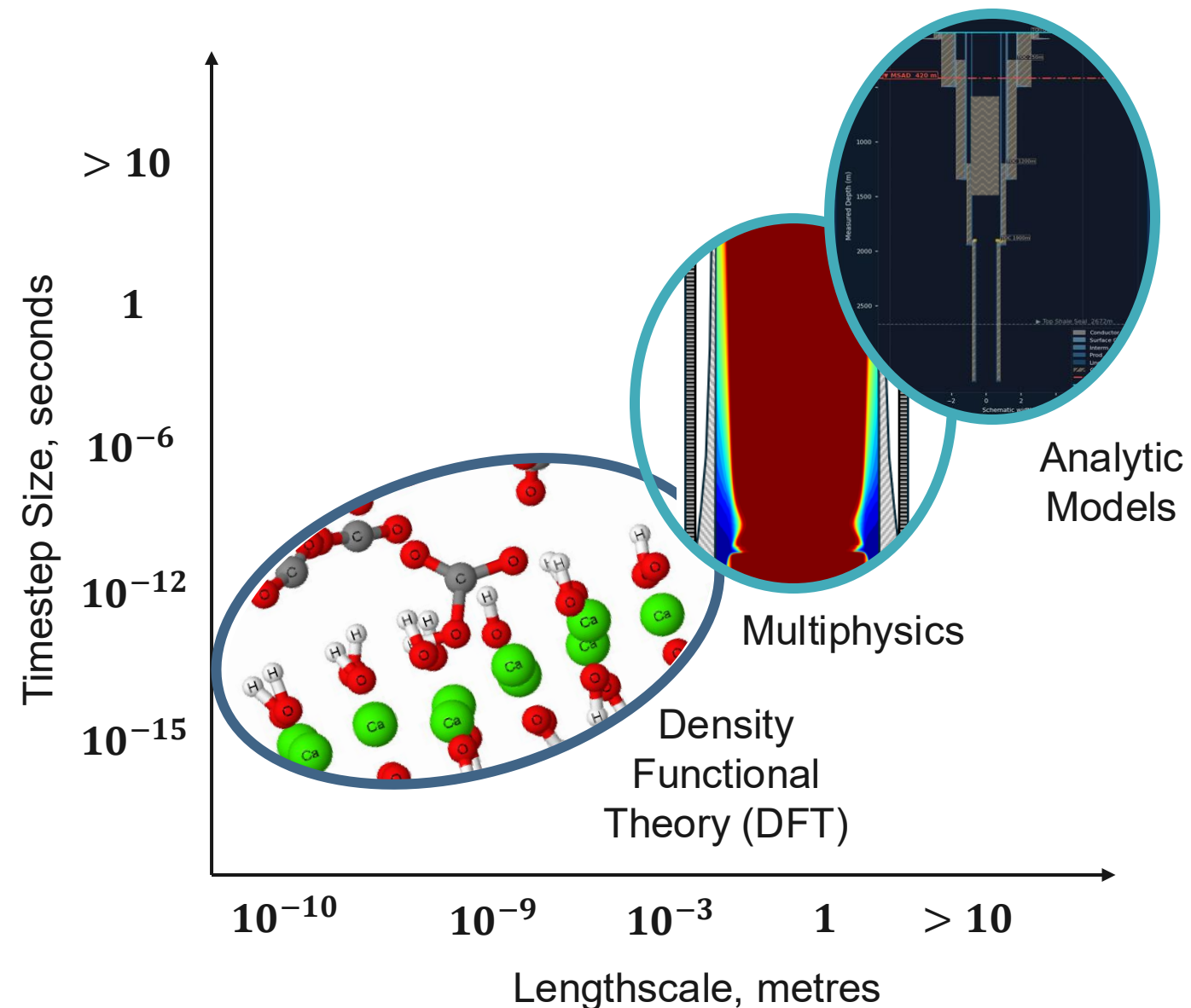
Mineral reactions

Mineral	Thermodynamic basis reaction	log K_{eq}	Surface-area function	Specific surface area ($m^2 g^{-1}$)	Rate constant ($mol m^{-2} s^{-1}$)	H^+ exponent, α
Calcite	$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	-8.48	Mineral mass	1.0	4.57×10^{-7}	0.08
Portlandite	$Ca(OH)_2(s) + 2H^+ \rightleftharpoons Ca^{2+} + 2H_2O$	22.81	Mineral mass	16.5	7.08×10^{-8}	0.18
CSH(1.8)	$CSH(1.8) + 3.6H^+ \rightleftharpoons 1.8Ca^{2+} + SiO_2(aq) + 7H_2O$	32.60	Mineral mass	45.0	7.94×10^{-11}	0.33
Amorphous silica	$SiO_2(am) \rightleftharpoons SiO_2(aq)$	-2.54	Mineral mass	1.0	1.0×10^{-10}	0.00

Aqueous secondary-species reactions

Species	Basis reaction	log K_{eq}
HCO_3^-	$CO_2(aq) + H_2O \rightleftharpoons H^+ + HCO_3^-$	-6.09
CO_3^{2-}	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	9.62
$CaCO_3(aq)$	$CaCO_3(aq) \rightleftharpoons Ca^{2+} + CO_3^{2-}$	-2.54
$CaHCO_3^+$	$CaHCO_3^+ \rightleftharpoons Ca^{2+} + HCO_3^-$	-1.11
$CaOH^+$	$CaOH^+ \rightleftharpoons Ca^{2+} + OH^-$	-0.45
OH^-	$OH^- + H^+ \rightleftharpoons H_2O$	13.30

So... What is DFT?



DFT is...

...the most accurate, *whilst* most computationally tractable, theory for predicating and estimating chemical properties.

- Atomic-scale - nanometres, nanoseconds, etc
- *Ab initio* / first principles - predicts behaviour from fundamental quantum mechanics, *without* fitting to experimental data*.
- Provides a *complementary* source of chemical data alongside experiments.

(*to the DFT purists reading this, I concede DFT has some empirical tuning with regards to hybrid xc-functionals, dispersion corrections etc but I feel that this statement is still valid in the context of simulation environments typical of this industry...)

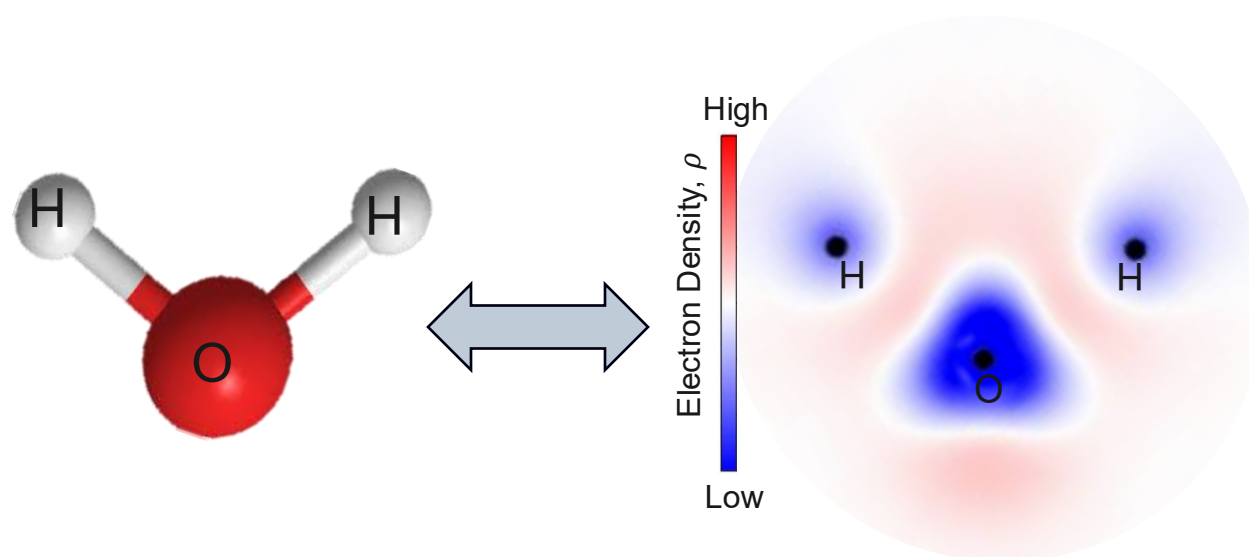
Energy is King...

Back in 1929, Paul Dirac captured the central promise—and challenge—of quantum chemistry:

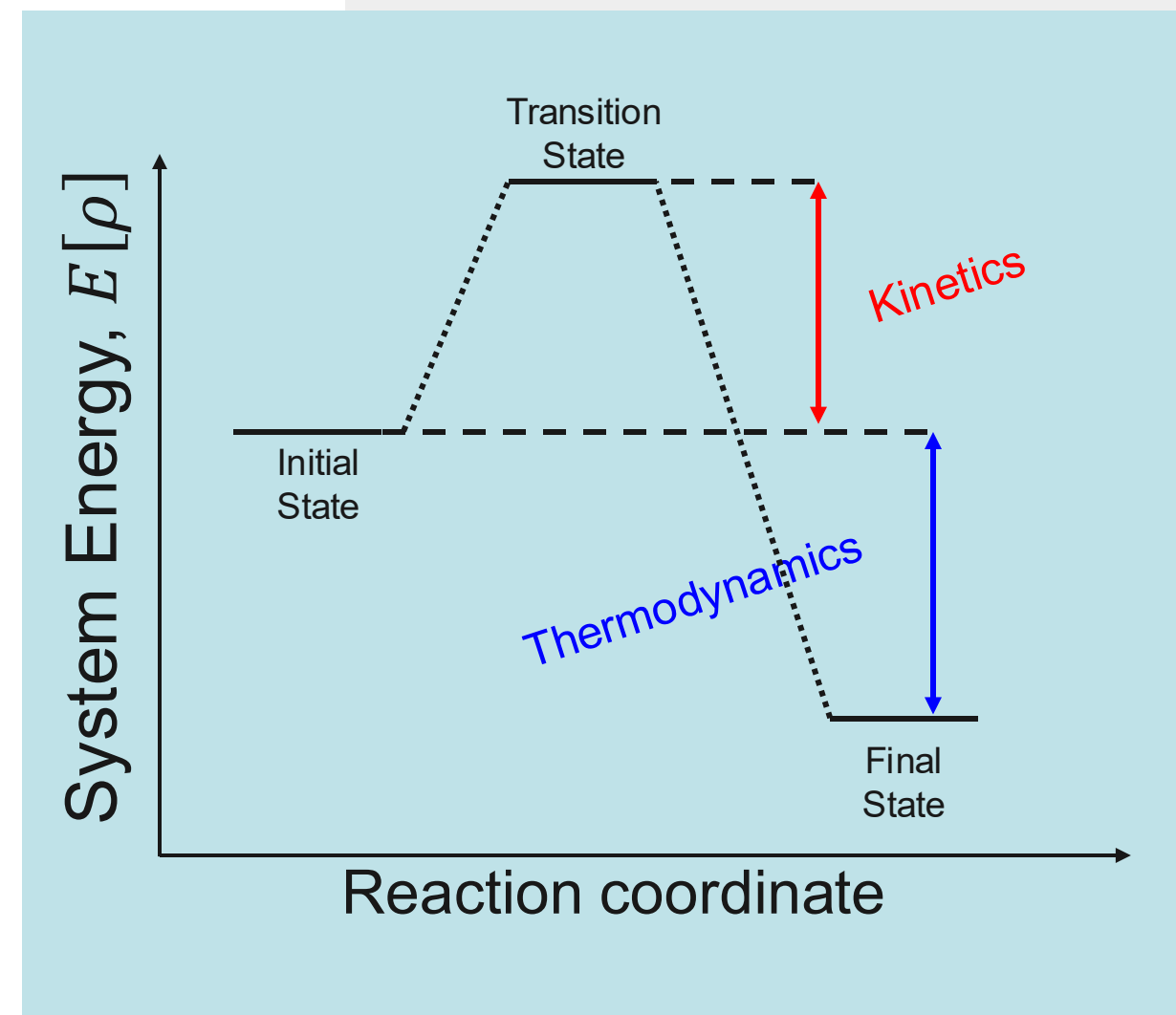
“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble...”

In essence, Schrödinger’s equation provides the quantum-mechanical framework needed to describe chemical systems. However, for *realistic* many-electron systems, solving the full wavefunction becomes computationally intractable.

DFT provides a practical way around this. Rather than describing the system through its full many-electron wavefunction, DFT rephrases the problem in terms of the electron density, which is far simpler to handle computationally. This makes it possible to estimate the system energy and electronic structure at a manageable cost, while still capturing the key changes in bonding associated with chemical reactions.



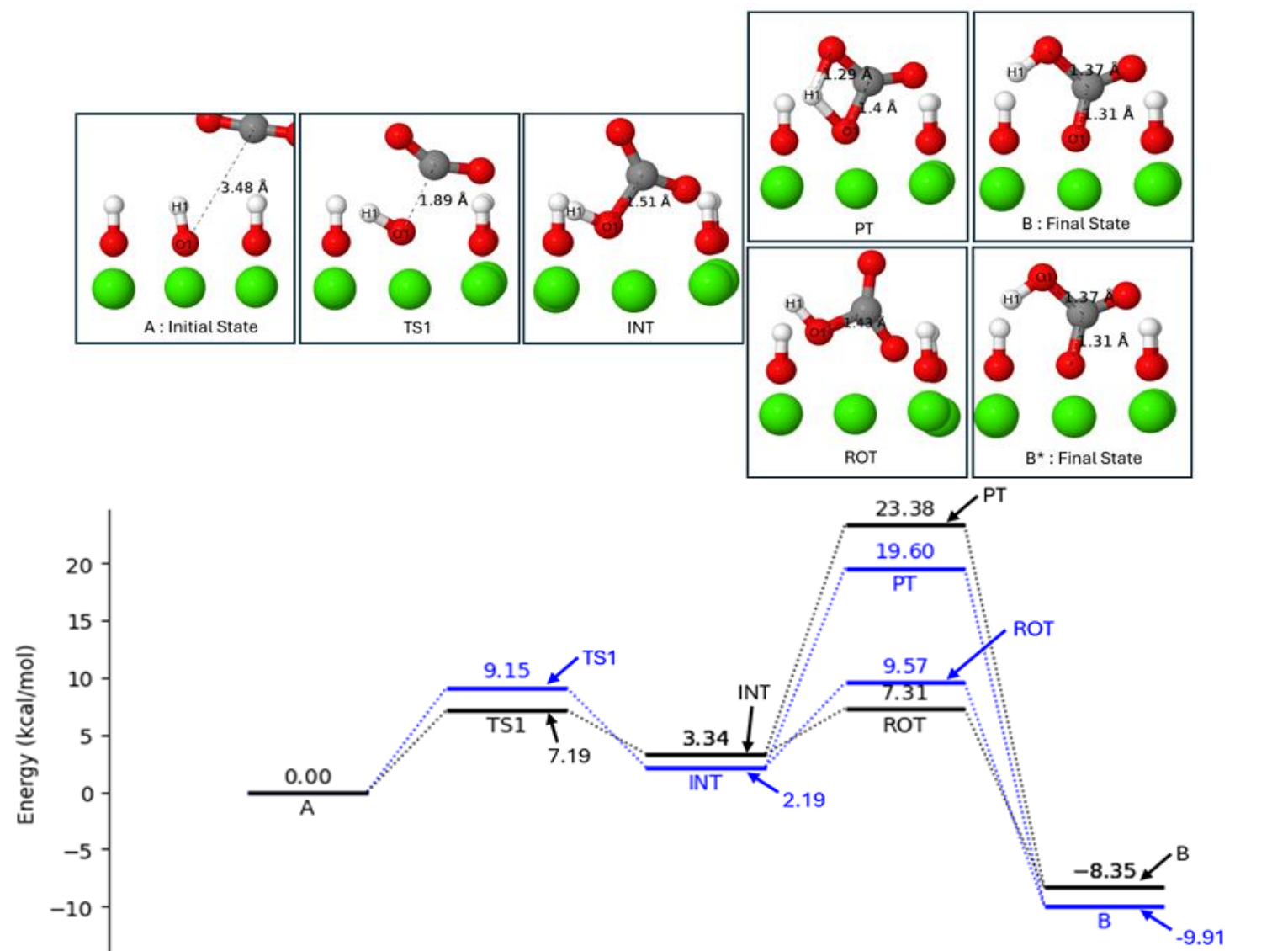
Above: illustration of a water molecule’s electron density distribution as solved by DFT.



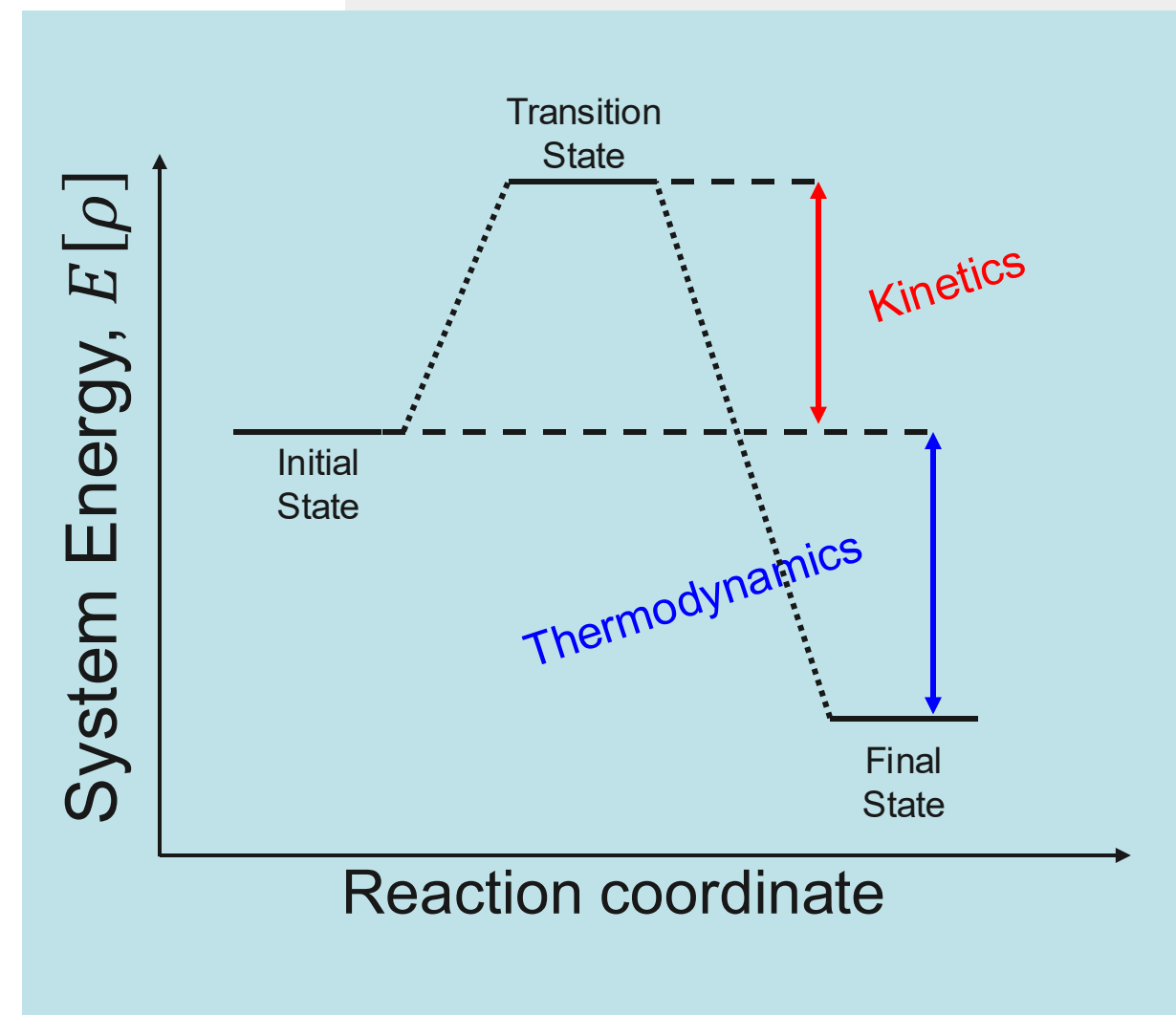
Above: a simplified* schematic of how one could interpret system energies to inform reaction kinetics and thermodynamics

(*to the DFT purists, I am aware that this schematic omits ZPE for static barriers, nor does this schematic translate directly to MTD. It is intended simply to illustrate the power of estimating a system’s energetic landscape from first principles..)

Energy is King...



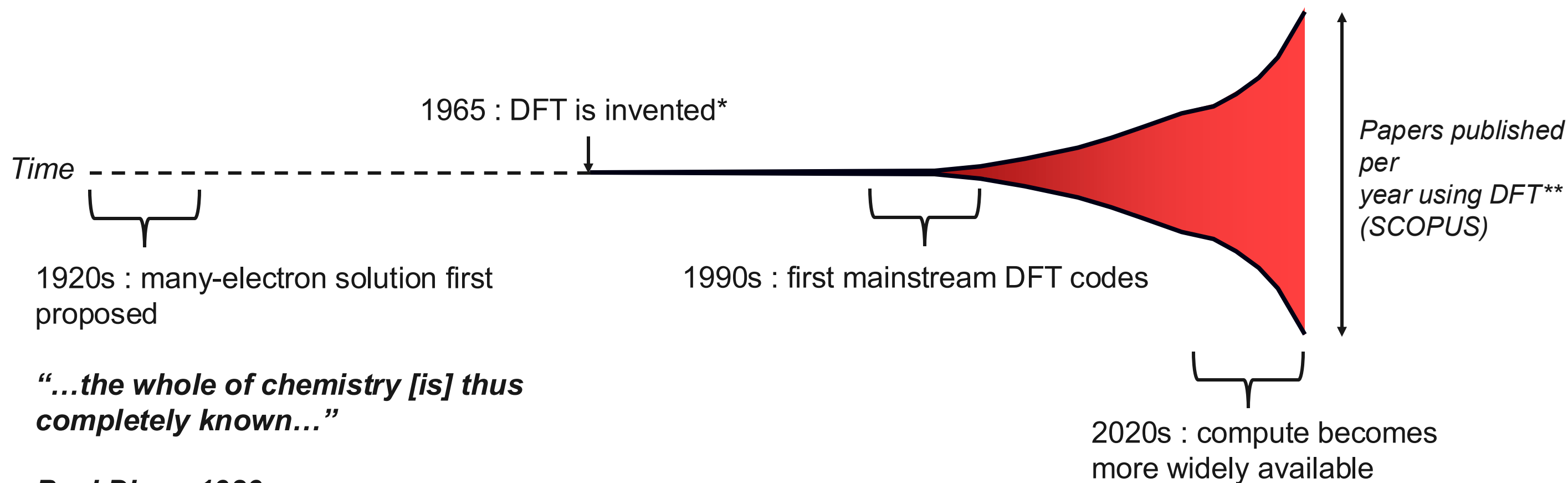
Above: a figure from a publication we have under review investigating portlandite carbonation. Pre-print available at: https://papers.ssrn.com/sol3/papers.cfm?abstract_id=7289882 "Density Functional Theory Investigation of Water-Mediated Portlandite Carbonation under CCS-Relevant CO₂ Exposure". Am currently working on revisions, contact me to discuss: james.hanson@elementalenergies.com



Above: a simplified* schematic of how one could interpret system energies to inform reaction kinetics and thermodynamics

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So.... Why now?

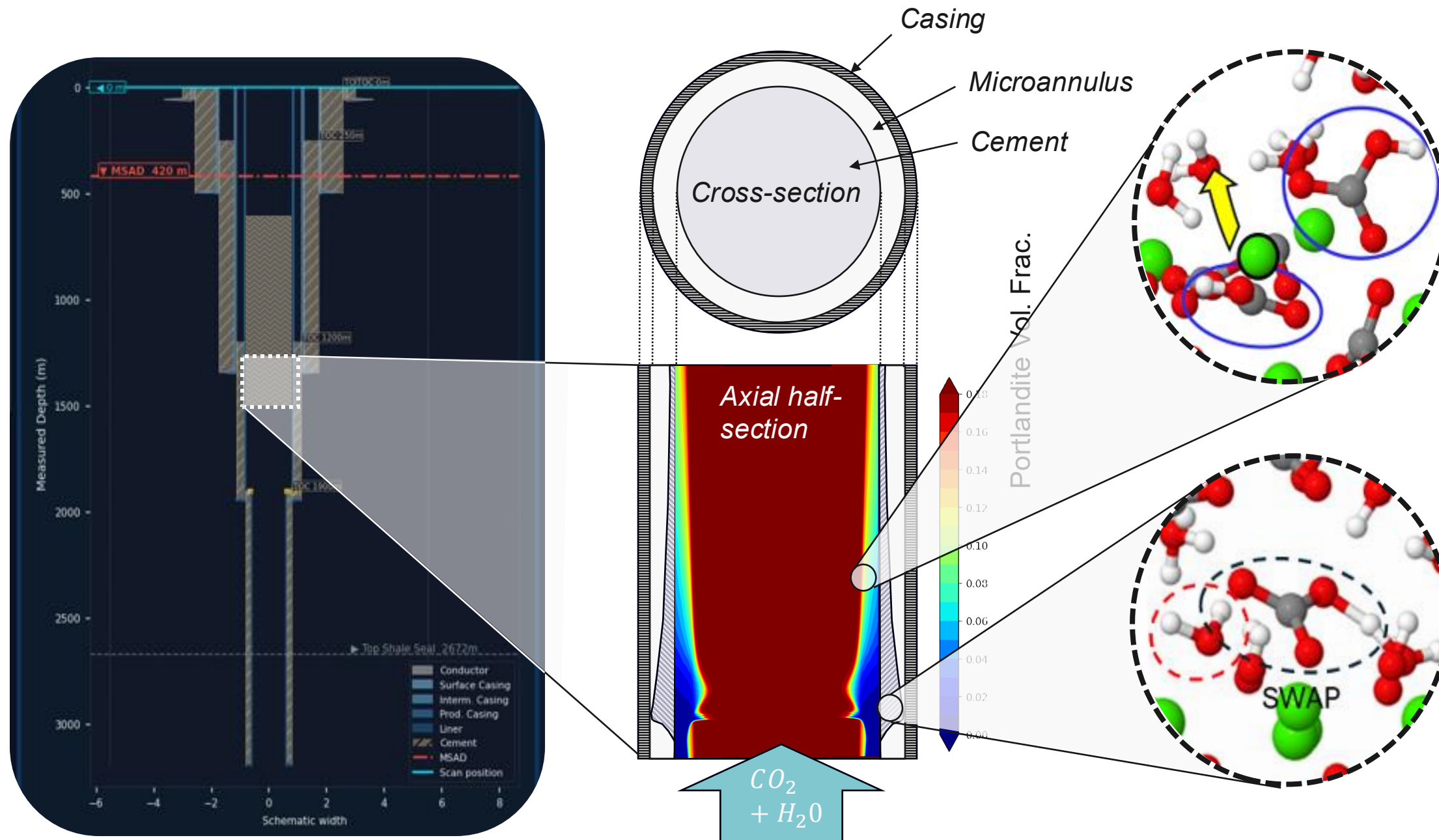


Above: a schematic illustrating the rapid growth in publications referring to DFT, based on results from SCOPUS.

*For those interested, I highly recommend David Clary's biography of Walter Kohn, one of the pioneers of DFT: "Walter Kohn: From Kindertransport and Internment to DFT and the Nobel Prize."

** "DFT" can refer to many things in the SCOPUS database. Hence, I used many keywords such as "quantum" OR "electron" OR "exchange" etc.

Looking to the future...



I think we are at the genesis of a really incredible period for science, where we can model these systems across the full range of scales: analytical, full-well models, through metre-scale reactant transport simulations, and right down to individual atoms and molecules.

In a five-minute TechByte I have not had the chance to cover some of the newer developments in molecular simulation, particularly machine-learned interatomic potentials, which are making atomistic modelling dramatically more computationally accessible. Taken together, these approaches are giving us the ability to connect behaviour across scales in ways that were simply not practical before.

Exciting times ahead...

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