Ab Initio Study of Hydrogen Quantum Tunnelling in NnVH Defects

Samuel J. Frost

University of Warwick

NnVH Defects in Diamond

- NnVH defects contain a central vacancy, surrounded by n substitutional nitrogens, where $n \in [0, 3]$, as well as a hydrogen sitting in the vacancy.
- The original proposed structure of these defects were the hydrogen being bonded to one of the unsaturated carbons surrounding the vacancy, giving rise to a low order point group. (NOT REALLY)
- EPR experiments observe a higher order point group, leading to the suspicion that the hydrogen was bonded to one of the nitrogens, however ab initio studies show that this is too energetically unfavourable.
- This lead to the theory that the hydrogen is rapidly reorientating *between* carbon atoms at a rate fast enough that it shows a higher order averaged symmetry when observed under EPR.
- Classical estimates for the reorientation give incredibly low rates for reorientation, with hydrogen staying at one carbon site for over 300s, much too slow to show averaged symmetry under EPR, which measures at rates in the GHz range. This is shown below in equation .
- This gave rise to the now widely accepted theory that the hydrogen is in fact *quantum tunnelling* between equivalent carbon sites.

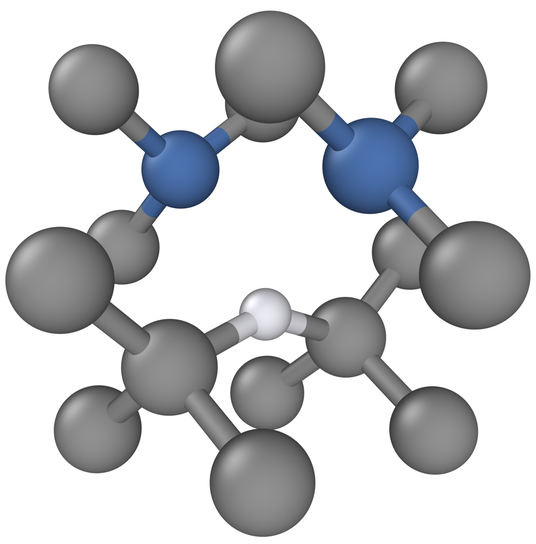

Figure 1. N_2VH in its averaged C_{2v} symmetry position, switching rapidly between the two central carbons. Hydrogen is shown in white, nitrogen in blue, and carbon in grey, most of the surrounding structure has been omitted for clarity. Generated using OVITO.

Attempt Frequency from Phonon Modes

- In order to calculator the tunnelling rate, the attempt frequency over the barrier must be known.
- This can be approximated as the vibrational frequency of hydrogen in the *direction* of the reaction coordinate, ν.
- **Finite displacement phonon calculations** were performed to calculate the phonon modes pertaining to each atom. A $3N \times 3N$ *dynamical matrix* is retrieved, which contains the force acted on each atom due to the displacement of another when moved a finite displacement from its minimum energy point.
- This can be represented mathematically by equation , where E is energy, r_n is the displacement(?) of an atom and m_n is its corresponding mass, where i and j occur for every possible pair of atoms.

$$\frac{\mathrm{d}^2 E}{\mathrm{d}r_i \, \mathrm{d}r_j} \frac{1}{\sqrt{m_i \, m_j}}$$

- From here we can diagonalise the matrix to retrieve its eigenvalues and eigenvectors, which detail the strength and direction of each phonon mode.
- The dot of product of these modes, with the normalised direction of the reaction coordinate will give the tunnelling frequency, ν.
- Due to the computational complexity of this take, only the calculation for the N_2VH defect was performed, however the vibrational frequency along the path was found to be $\nu = 1363.5\,\mathrm{cm}^{-1}$.
- This is remarkably close to the one phonon mode of the diamond lattice, $1332\,\mathrm{cm}^{-1}$, a value which has previously been used as an estimate for the attempt frequency, giving a good justification for its further use in this work. Using either value gives no meaningful difference to the results for N_2VH.

Computational Details

- All calculations were performed using CASTEP 23.1, using a periodic 64 atom simulation cell.
- The meta-GGA RSCAN functional was used for all calculations unless stated otherwise.
- A plane wave cut-off of $1\,000$ eV and a $4 \times 4 \times 4$ monkhorst-pack k-point grid was used, with a force tolerance of 0.02 eV / Å for geometrical minimisation.
- A lattice constant of 3.5537 was found during convergence testing, close to the experimental value of 3.567.

Probability of Tunnelling

- **Nudged Elastic Band (NEB)** calculations were performed to find the energy along the reaction coordinate of the tunnelling hydrogen for each NnVH system.
- **Gaussian Process Regression** was employed to interpolate between the discrete points along the reaction coordinate such that continuous integration could be performed later.
- **The WKB approximation** was then used to calculate the instantaneous probability of tunnelling.

$$P = \exp\left(\frac{-4\pi}{h} \int_a^b \sqrt{2m\,(V - E)}\right)$$

In this equation, the integral is performed between the *turning points* of the energy barrier, a and b, where the potential and energy of the system are equal, such that $V = E$. It is not *only* the hydrogen that moves when quantum tunnelling is taking place, the atoms neighbouring the vacancy also account for a small amount of movement (around 10% of the total displacement). Therefore, when calculating the mass, we can consider their mass in proportion to their contribution to the reaction coordinate.

$$\frac{1}{m^*} = \sum_i \frac{1}{m_i} \frac{\Delta r_i}{q}$$

Where m^* is the effective mass, Δr_i is the total displacement of atom i, and q is the total displacement of the reaction coordinate, such that $\sum_i \frac{\Delta r_i}{q} = 1$

Really, we need to go ahead and calc dx/dq, and do $1/ = (1/mi) * (xi/q)^2$ We just decided that the number for distance that ASE gives us is too strange to reliably use since we can't reproduce it Actually I think our errors might be from pbc -> use find_mic maybe? copy from source TODO: USE FIND-MIC TO GET REPRODUCABLE PATH VALUE USE THAT VALUE TO THEN GET THE REDUCED MASS OF TUNNELLING BY FINDING DX/DQ LOOK INTO FIXING THE TEMPERATURE RESULTS, BUT 0K MAY JUST HAVE TO BE FINE

Energy Levels

Although anharmonic effects are most likely present, the hydrogen atom can be approximated as a quantum harmonic oscillator (QHO), this means that the ground state energy (*i.e.* the energy at 0K) would be

$$E = \frac{1}{2} h\nu$$

We have multiple phonon modes, with different strengths pointing in the direction of the hydrogen atom. Taking the sum of all these modes can give us an estimate for the vibrational frequency in that direction.

$$\sum_i \frac{1}{2} h\nu_i + h\nu_i \frac{1}{\exp^{h_i \nu / kBT} - 1}$$

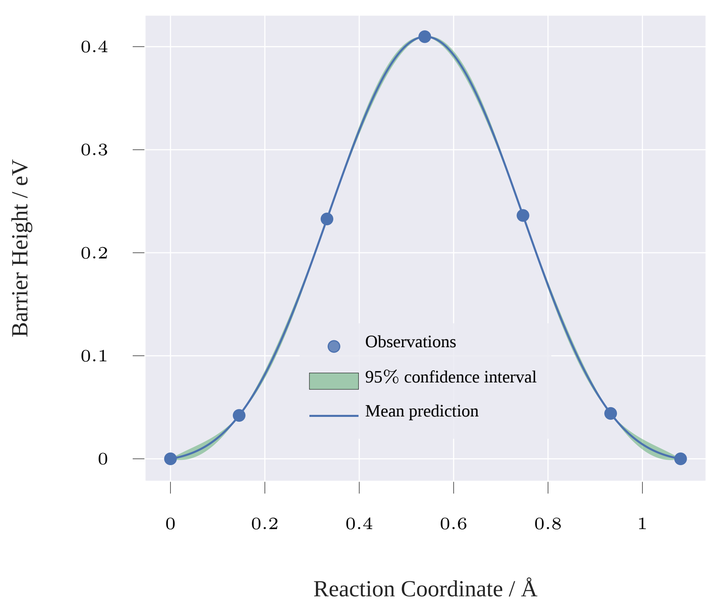

Figure 2. This is the caption of the graph

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Calculated Rates for Every Possible Defect

Previous studies have calculated the ab initio energy barrier for every viable NnVH defect, however they have not used those results to fully calculate the reorientation rate of the Hydrogen when possible. The original ab inito results are compared to literature, along with a full calculation of the reorientation rate.

Defect		Barrier / eV	Lit. / eV	Rate @ 0K / GHz
VH^0	$S = 3/2$	0.379	0.6	0
NVH^0	$S = 0$	0.926	1.1	0
NVH^0	$S = 1$	0.572	0.5	0
NVH^-	$S = 1/2$	0.410	0.5	0
NVH^+	$S = 1/2$	0.607	0.6	0
N_2VH^0	$S = 1/2$	0.677	0.9	0
N_2VH^-	$S = 0$	0.157	0.1	0
N_2VH^+	$S = 0$	0.613	0.5	0

Table 1. Comparison of the different quantum tunnelling energy barriers for different NnVH defects in diamond, along with their comparison to previous ab initio studies. The rates at two different temperatures are calculated for each defect with the methods previously shown.

References

[1] Claude E. Shannon. A mathematical theory of communication. *Bell System Technical Journal*, 27(3):379–423, 1948.

https://www.samuelfrost.co.uk

Samuel.Frost@Warwick.ac.uk