Nudged Elastic Band Method to Study NnVH Defects and Vacancy Migration

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Nudged Elastic Band (NEB)

- Computational method to find the **Minimum Energy Path** (MEP) between two different states.
- A series of images are joined by springs, when each image is minimised it pushes the other images along the reaction coordinate, maintaining equal spacing.

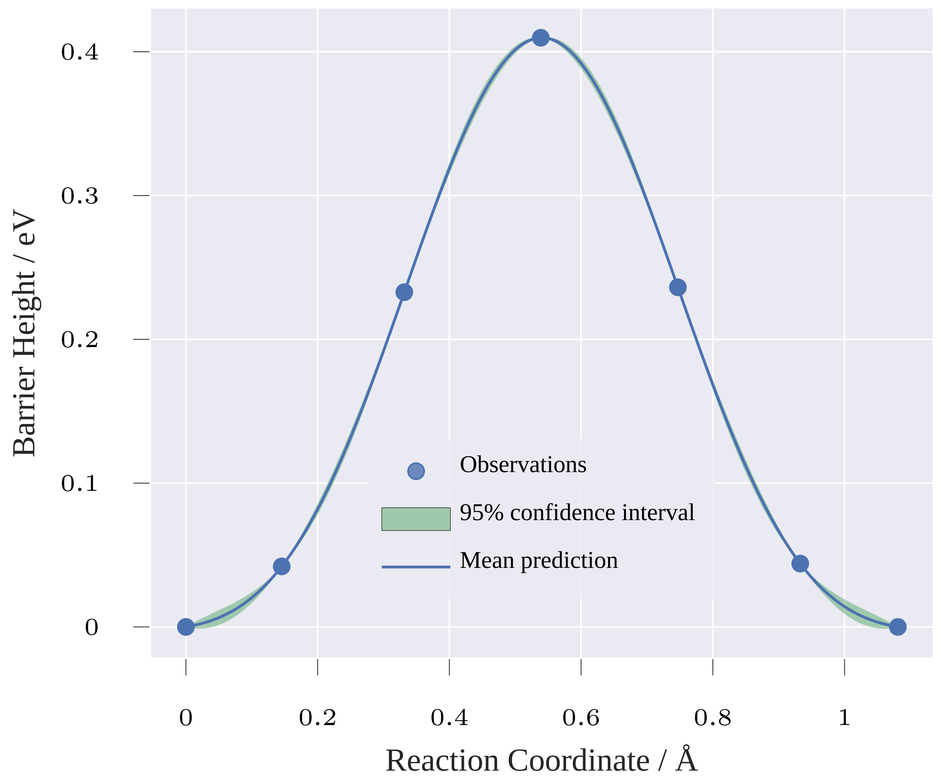

Figure 1. The NEB plot of the NVH^0 S=$\frac{1}{2}$ defect, showing the cumulative displacement of the minimum energy path on the x-axis, and the potential energy, or barrier height, on the y-axis. The shape is typical of every NnVH defect. Gaussian Process Regression has been used to interpolate along the path.

NnVH Defects in Diamond

- NnVH defects in diamond are made up of n substitutional **N**itrogens, where $n = 0, 1, 2, 3$, surrounding a **V**acancy, with a **H**ydrogen sitting in the vacancy.
- Defects show higher order symmetry under EPR, too unstable to just sit in the middle, so must be reorienting.
- Can calculate the energy barrier using NEB method. Classical rates are much too slow, so it must be quantum tunnelling!

$$\Gamma = \exp\left(\frac{E_a}{k_B T}\right) \approx 10^{-3}\,\text{GHz}$$

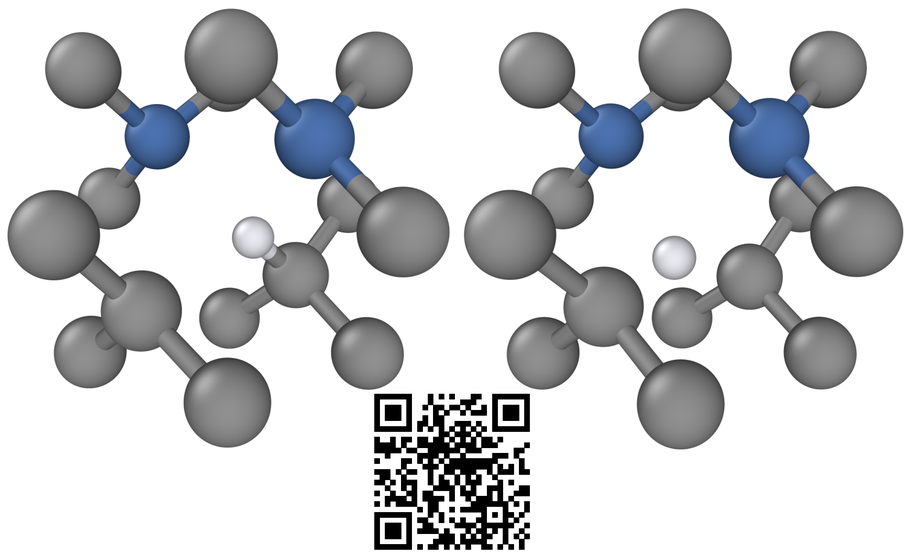

Figure 2. N_2VH in its C_{1h} position, and its averaged C_{2v} symmetry. Hydrogen is shown in white, nitrogen in blue, and carbon in grey, most of the surrounding structure has been omitted for clarity. Generated using OVITO [4].

Tunnelling Probability

- A **finite displacement** calculation retrieves a *dynamical matrix* that contains the force created on all N atoms due to the displacement of each atom from its origin. This can be used to find the vibrational frequency ν of each atom.

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

- The **WKB Approximation** is used to calculate the probability, P, of tunnelling through the potential energy barrier by integrating over the reaction coordinate, q.

$$E(\nu, T) = h\nu\left(\frac{1}{2} + \frac{1}{e^{h\nu/k_B T} - 1}\right)$$

$$\Gamma = \nu \exp\left(\frac{-4\pi}{h}\int_a^b \sqrt{2\mu\,(V(q) - E(T))}\,\mathrm{d}q\right)$$

Computational Details

- All DFT calclations were performed using CASTEP 23.1 [1], using a periodic 64 atom simulation cell and the meta-GGA RSCAN functional [5].
- A plane wave cut-off of $1\,000$ eV and a $4 \times 4 \times 4$ Monkhorst-Pack k-point grid was used on a 64 atom unit cell, with a force tolerance of 0.02 eV / Å for geometrical minimisation.
- An ACE Carbon potential [3] was used for all Molecular Dynamics simulations.

To Tunnel or not to Tunnel

- If the tunnelling rate is an order of magnitude lower than the EPR rate then it will show an averaged symmetry. So if the rate is 1 GHz then it will be averaged in X-band EPR [2].

Defect		Barrier / eV	MEP / Å	Rate / GHz		
				0 K	100 K	300 K
VH^0	$S = 3/2$	0.378	0.970	0.9715	39.39	12770
VH^-	$S = 1$	0.707	1.12	1e-4	0.0059	2.580
VH^+	$S = 0$	0.995	1.23	1e-7	8.3e-6	0.0050
NVH^0	$S = 0$	0.926	1.21	4e-7	3e-5	0.0196
NVH^0	$S = 1$	0.572	1.08	0.0043	0.2309	87.36
NVH^-	$S = 1/2$	0.410	1.08	0.00257	2.170	2306
NVH^+	$S = 1/2$	0.607	1.13	07e-4	0.0414	24.05
N_2VH^0	$S = 1/2$	0.677	1.12	4e-4	0.0247	10.21
N_2VH^-	$S = 0$	0.157	0.860	301.5	ν	ν
N_2VH^+	$S = 0$	0.613	1.15	2e-4	0.0142	11.04

Table 1. Comparison of the different tunnelling rates of every NnVH defect at various temperatures.

Vacancy Migration to the Surface

- Can use NEB to find the energy barriers for a vacancy moving to the surface.

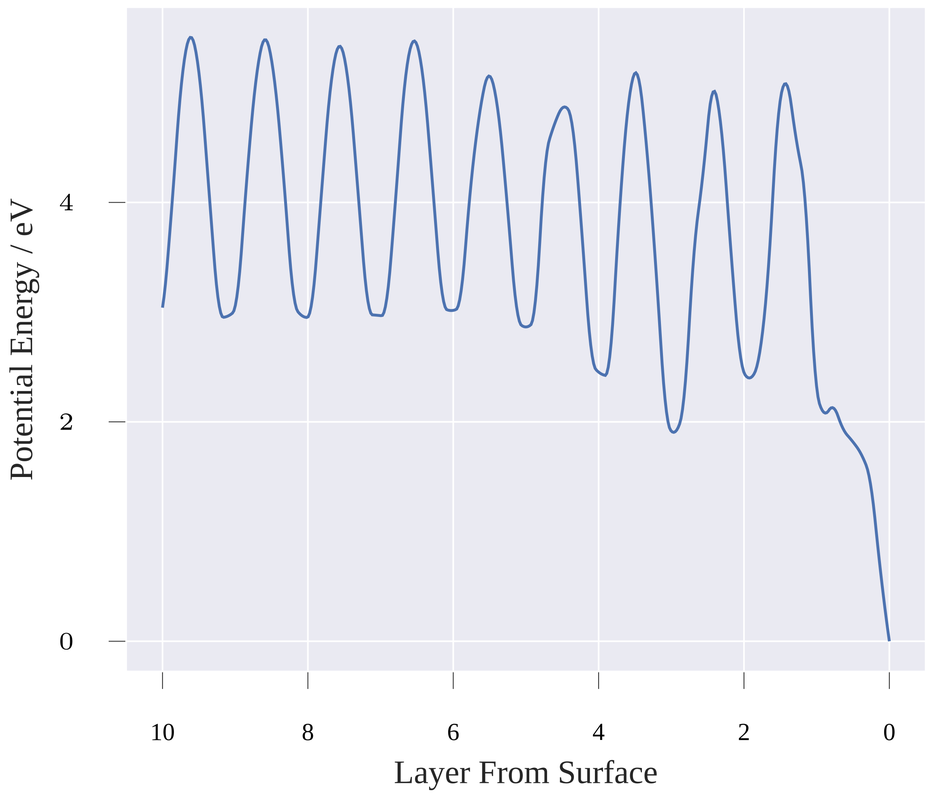

Figure 3. The combined NEB paths of a vacancy moving towards the surface from the bulk of an $1\,800$ atom unit cell, calculated using an ACE potential [3].

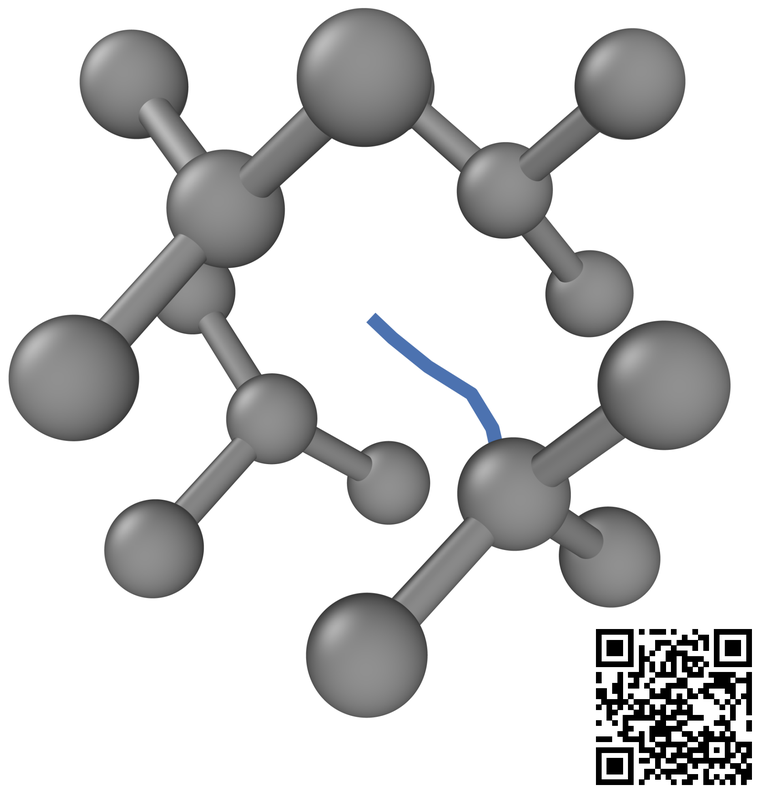

Figure 4. The path of a carbon atom switching places with a vacancy in bulk diamond calculated using DFT, notice the crooked path the carbon atom takes. Generated using OVITO [4].

References

[1] Stewart J Clark, Matthew D Segall, Chris J Pickard, Philip J Hasnip, Matt J Probert, Keith Refson, and Mike C Payne. First principles methods using castep. *Zeitschrift für Kristallographie*, 220(5-6):567–570, 2005.

[2] Jonathan Goss, Patrick Briddon, R Jones, and S Sque. The vacancy-nitrogen-hydrogen complex in diamond: A potential deep centre in chemical vapour deposited material. *Journal of Physics: Condensed Matter*, 15:S2903, 09 2003.

[3] Minaam Qamar, Matous Mrovec, Yury Lysogorskiy, Anton Bochkarev, and Ralf Drautz. Atomic cluster expansion for quantum-accurate large-scale simulations of carbon. *Journal of Chemical Theory and Computation*, 19(15):5151–5167, 2023. PMID: 37347981.

[4] Alexander Stukowski. Visualization and analysis of atomistic simulation data with ovito-the open visualization tool. *Modelling and Simulation in Materials Science and Engineering*, 18(1), JAN 2010.

[5] Jianwei Sun, Adrienn Ruzsinszky, and John P. Perdew. Strongly constrained and appropriately normed semilocal density functional. *Phys. Rev. Lett.*, 115:036402, Jul 2015.