


# Estimates of Quantum Tunneling Effects for Hydrogen Diffusion in PuO<sub>2</sub>

## Supplementary Information

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### 1. Details regarding our DFTB parametrization

The following text summarizes the ChIMES force field used for part of this work. The text is largely taken from Ref. 1. Similar to previous work[2], for Pu interactions we have used a wavefunction compression radius of 4.5 au for the s, p, and d-orbitals and a compression radius of 4.0 au for the f-orbitals, though in this case we use a density compression radius of 6.0 au. Once again we place a partial occupancy of 0.4 in the 6d-orbitals. DFTB+ is parameterized with Slater type orbitals for all elements. We have found that the underlying parameterization is largely insensitive to the choice of exponential coefficients[2].

### 2. The Chebyshev Interaction Model for Efficient Simulation (ChIMES)

The design philosophy behind ChIMES involves mapping quantum mechanical energies onto linear combinations of many-body Chebyshev polynomials of the first kind. Chebyshev polynomials of the first kind have a number of desirable properties for creation of interatomic potential energy surfaces, including: (i) they are orthogonal (with respect to a weighting function) and can be generated recursively, allowing for basis set completeness and user defined complexity, (ii) higher order polynomials tend to have decreasing expansion coefficient values (due to their monic form), and (iii) they are “nearly optimal” (the error in an expansion will closely resemble a minimax polynomial). In addition, derivatives of Chebyshev polynomials of the first kind are related to Chebyshev polynomials of the second kind, which themselves are orthogonal and can be generated recursively. This allows for easy and reliable determination of forces and stress tensor components for atomistic calculations.

Briefly, the ChIMES total energy corresponds to an  $n$ -body expansion:

$$E_{n_B} = \sum_{i_1}^{n_a} {}^1E_{i_1} + \sum_{i_1 > i_2}^{n_a} {}^2E_{i_1 i_2} + \sum_{i_1 > i_2 > i_3}^{n_a} {}^3E_{i_1 i_2 i_3} + \cdots + \sum_{i_1 > i_2 \dots i_{n_B-1} > i_{n_B}}^{n_a} {}^{n_B}E_{i_1 i_2 \dots i_{n_B}}, \quad (1)$$

where  $E_{n_B}$  is the total ChIMES system energy,  $n_B$  is the maximum bodiedness,  ${}^nE_{i_1 i_2 \dots i_n}$  is the  $n$ -body ChIMES energy for a given set of atoms with indices  $i = \{i_1, i_2, \dots, i_n\}$ , and  $n_a$  is the total number of atoms in the system. The one-body energies,  ${}^1E_{i_1}$ , correspond to the atomic energy constants for each element type.

The two-body (pairwise) energies are expressed as linear combinations of Chebyshev polynomials of the first kind:

$${}^2E_{i_1 i_2} = f_p(r_{i_1 i_2}) + f_c^{e_{i_1} e_{i_2}}(r_{i_1 i_2}) \sum_{m=1}^{O_2} C_m^{e_{i_1} e_{i_2}} T_m(s_{i_1 i_2}^{e_{i_1} e_{i_2}}) \quad (2)$$

In this case,  $T_m(s_{i_1 i_2}^{e_{i_1} e_{i_2}})$  represents a Chebyshev polynomial of order  $m$ , and  $s_{i_1 i_2}^{e_{i_1} e_{i_2}}$  is the pair distance transformed to occur over the interval  $[-1, 1]$  using a Morse-like function[3,4] (See Ref. 5 for details). Here,  $s_{i_1 i_2}^{e_{i_1} e_{i_2}} \propto \exp(-r_{i_1 i_2}/\lambda_{e_1 e_2})$  and  $\lambda_{e_1 e_2}$  is an element-pair distance scaling constant, usually taken to be the peak position of the first coordination shell.  $C_m^{e_{i_1} e_{i_2}}$  is the corresponding permutationally invariant coefficient for the interaction between atom types  $e_{i_1}$  and  $e_{i_2}$ , taken from the set of all possible element types,  $\{e\}$ . The term  $f_c^{e_{i_1} e_{i_2}}(r_{i_1 i_2})$  is a Tersoff cutoff function[6] which is set to zero beyond a maximum distance defined for a given  $\{e_1, e_2\}$  pair set. In order to prevent sampling of  $r_{i_1 i_2}$  distances below what is sampled in our DFT training set, we introduce use of a smooth penalty function  $f_p(r_{i_1 i_2})$ . We refer the reader to previous work for additional details[7].

We can now create a greater than two-body orthogonal basis set by taking products of the  $\binom{n}{2}$  unique constituent pairwise polynomials of the higher order terms. In other words, a three-body term has  $\binom{3}{2} = 3$  pairs, which yields the following expression for the ChIMES three-body energy:

$${}^3E_{i_1 i_2 i_3} = f_c^{e_{i_1} e_{i_2}}(r_{i_1 i_2}) f_c^{e_{i_1} e_{i_3}}(r_{i_1 i_3}) f_c^{e_{i_2} e_{i_3}}(r_{i_2 i_3}) \sum_{m=0}^{\mathcal{O}_3} \sum_{p=0}^{\mathcal{O}_3} \sum_{q=0}^{\mathcal{O}_3'} C_{mpq}^{e_{i_1} e_{i_2} e_{i_3}} T_m(s_{i_1 i_2}^{e_{i_1} e_{i_2}}) T_p(s_{i_1 i_3}^{e_{i_1} e_{i_3}}) T_q(s_{i_2 i_3}^{e_{i_2} e_{i_3}}). \quad (3)$$

We take a triple sum for the  $i_1 i_2$ ,  $i_1 i_3$ , and  $i_2 i_3$  polynomials over the hypercube up to  $\mathcal{O}_3$ , and include a single permutationally invariant coefficient for each set of powers and atom types,  $C_{mpq}^{e_{i_1} e_{i_2} e_{i_3}}$ . We use the primed sum to denote that only terms for which two or more of the  $m, p, q$  polynomial powers are greater than zero are included in order to guarantee that three distinct atom-centers are evaluated. The expression for  ${}^3E_{i_1 i_2 i_3}$  also contains the  $f_c$  smoothly varying cutoff functions for each constituent pair distance. Penalty functions are not included in this case and instead are handled entirely by the two-body interaction. Similarly, the four-body energy can be written as a product of the  $\binom{4}{2} = 6$  unique pairwise interactions, though these were not sampled in this work.

Optimal ChIMES parameters (the coefficients of linear combination) can then readily be determined through the overdetermined matrix equation  $AC = B_{\text{rep}}$ . The matrix  $A$  corresponds to the values of the requisite polynomials for a given training configuration, or in other words the derivatives with respect to the fitting coefficients. The column vectors  $C$  and  $B_{\text{rep}}$  correspond to the linear ChIMES coefficients and the numerical values for the training set, respectively.

### 3. Determination of the DFTB repulsive energy from ChIMES

The ChIMES training set was determined by computing DFTB forces ( $F$ ) and diagonal stress tensor components ( $\sigma$ ) for each configuration with the chosen set of Hamiltonian parameters with zero values for those components from  $E_{\text{Rep}}$ . These “repulsive energy free” results were then subtracted from the DFT values for those quantities, i.e.,

$$\begin{aligned} F_{\text{Rep}\alpha_i}^{\tau*} &= F_{\text{DFT}\alpha_i}^{\tau} - F_{\text{QM,DFTB}\alpha_i}^{\tau} \\ \sigma_{\text{Rep}\alpha\alpha}^{\tau*} &= \sigma_{\text{DFT}\alpha\alpha}^{\tau} - \sigma_{\text{QM,DFTB}\alpha\alpha}^{\tau} \end{aligned} \quad (4)$$

Here,  $\tau$  corresponds to a specific MD configuration,  $\alpha$  to the cartesian direction, and  $i$  is the atomic index. The ‘\*’ is used to denote that the quantities being computed are part of the training set, and ‘QM,DFTB’ refers to the quantum components of the DFTB calculation, i.e., only forces and stresses from  $E_{\text{BS}}$  and  $E_{\text{Coul}}$ . Inclusion of configurational total energies generally resulted in minimal impact on quality of the  $E_{\text{Rep}}$  fit and were thus excluded from

our training data, similar to previous efforts[1,2]. This results in the following objective function:

$$F_{obj} = \sqrt{\frac{1}{N_d} \left( \sum_{\tau=1}^M \sum_{i=1}^N \sum_{\alpha=1}^3 \left[ F_{\text{ChIMES}_{\alpha i}}^{\tau} - F_{\text{Rep}_{\alpha i}}^{\tau*} \right]^2 + \sum_{\tau=1}^M \sum_{\alpha=1}^3 \left[ \sigma_{\text{ChIMES}_{\alpha\alpha}}^{\tau} - \sigma_{\text{Rep}_{\alpha\alpha}}^{\tau*} \right]^2 \right)}, \quad (5)$$

where  $M$  is the total number of configurations in the training set, and  $N_d$  is the total number of data entries ( $3MN$  force components plus  $3M$  stress tensor components).

#### 4. ChIMES hyperparameters for H/PuO<sub>2</sub>

Two-body ChIMES interactions were truncated at 12th order and three-body interactions at 8th order, similar to our previous efforts. All minimum and cutoff radii for the ChIMES  $E_{\text{Rep}}$  were set to include the first coordination shell sampled in our training set, only:  $3.2 \leq r_{\text{PuPu}} \leq 4.2 \text{ \AA}$ ,  $1.85 \leq r_{\text{PuO}} \leq 2.85 \text{ \AA}$ , and  $1.75 \leq r_{\text{PuH}} \leq 4.05 \text{ \AA}$ . We use values of  $\lambda_{\text{PuPu}} = 3.75 \text{ \AA}$ ,  $\lambda_{\text{PuO}} = 2.25 \text{ \AA}$ , and  $\lambda_{\text{PuH}} = 2.25 \text{ \AA}$  for the Morse-like coordinate transforms and a value of  $0.5 r_{\text{max}}$  for the onset of the Tersoff cutoff function. H-H, O-H, and O-O repulsive interaction were not sampled in our training set and were thus taken from the miomod-hh-0-1 and mio-1-1 parameter sets.

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