

Parahydrogen Properties Version 05 Database Release for Nuclear Thermal Propulsion Applications

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Consistent modeling assumptions across any large project are crucial to minimize errors between different approaches. Use of consistent material and fluid properties across a large project supports consistent interpretation and application within modeling and simulation results as well as their relevancy to operational systems. NASA's Space Nuclear Propulsion program dedicates extensive resources towards establishing consistent and, to the extent possible, accurate property databases for its internal staff and all external partners. This work highlights the extensive research performed to modernize the fluid property database of hydrogen which is the leading propellant option for in-space nuclear propelled spacecraft. Specifically, the parahydrogen spin state is of interest since the propellant is stored in a near normal boiling point liquid state which results in it consisting almost entirely of the parahydrogen spin isomer. This database tool has taken recent NASA work and modernized it into a python-based package for easy usage across all modeling entities. The package allows users to provide temperature and pressure pairs along with their desired output properties to yield results accounting for both real-gas and equilibrium dissociation effects while also sharing the default thermodynamic reference state provided by the National Institute of Standards and Technology (NIST) Standard Database 23. The suite also includes advanced capabilities to increase usability, such as on-the-fly interpolation and multidimensional plotting.

I. INTRODUCTION AND MOTIVATIONS

To enable crewed, cargo, and science missions to Mars and beyond, the National Aeronautics and Space Administration (NASA) is investigating space nuclear propulsion (SNP) technology to provide the performance requirements necessary for efficient flight time. Nuclear thermal propulsion (NTP) is a prominent option that relies on superheating a light working fluid, typically hydrogen, from cryogenic temperatures (~20 K) to upwards of 3000 K to reach achievable engine specific impulse (I_{sp}). Additionally, fluid pressure can range from ~0 Pa to 30 MPa depending on the engine configuration. This wide range of temperatures and pressures creates a need for high-fidelity parahydrogen properties at all states and locations within the engine system. This work allows users to calculate necessary thermophysical and transport

properties between 0 – 100 MPa and ~20 – 6000 K. Expansion of the dataset to these ranges beyond the desired application removes the need for data extrapolation while limiting inaccuracies in the virial equation of state at extremely high pressures and avoiding the inclusion of ionization effects at extremely high temperatures and low pressures.

In its cryogenic state, the spin states of the two hydrogen atoms follow a singlet form indicative of parahydrogen¹. While the atomic mass does not change, the thermophysical and transport properties of dihydrogen differ significantly with spin state for temperatures below roughly 600 K. The National Institute of Standards and Technology (NIST) models for parahydrogen have a temperature limit of 1000 K which does not cover the range observed in the reactor fuel channels and nozzle⁴. Past work performed under NASA's SNP Modeling and Simulation (M&S) efforts extended the accepted NIST parahydrogen model in a similar manner to this new work but instead executed via Mathcad 15 worksheets^{2,3}. This earlier database is referred to as the version 03b suite. Efforts to modernize the property calculators into Python due to permanent deactivation of Mathcad 15 for all licensees as well as for open-source availability of this software language and its extensive, readily available mathematical and optimization toolkits. Implementation of the Mathcad approach in Python created a need for high-fidelity verification between the two software tools along with identification and mitigation of any errors.

The goal of this tool is to create a consistent fluid property assumption for all government and industry NTP system modelers to remove systematic error when comparing results. The primary end use case of the suite is for users to generate tabulated temperature- and pressure-dependent fluid properties to fit their specific application. Following code translation from Mathcad to Python, additional capabilities have been added to the code suite to remove identified errors from the version 03b database and to handle more unique user applications, such as on-the-fly, highly accurate property interpolation and multidimensional plotting. This work will also introduce the bridging parameters methodology to connect the high-temperature properties (>1500 K) with a better prediction of the point of dissociation (<1000 K) since REFPROP

does not include this physics in its parahydrogen property database. This finalized property database is coined as the version 05 release. Included in version 05 are the following properties:

TABLE I. List of Available Fluid Properties with Units

Available Properties	Units
Dihydrogen Mole Fraction	[-]
Specific Volume, v	$\frac{m^3}{kg}$
Enthalpy, h	$\frac{J}{kg}$
Entropy, s	$\frac{J}{kg * K}$
Equilibrium and Frozen Isobaric Specific Heat, C_p	$\frac{J}{kg * K}$
Equilibrium and Frozen Isochoric Specific Heat, C_v	$\frac{J}{kg * K}$
Sound Speed, a	$\frac{m}{s}$
Equilibrium and Frozen Thermal Conductivity, k	$\frac{W}{m * K}$
Viscosity, μ	$Pa * s$

II. MODERNIZATION METHODOLOGY

II.A. Mathcad to Python Translation

One of the primary goals of this work was to translate the calculation schemes from the decommissioned Mathcad 15 tool to an open-source software that more engineers and scientists are familiar with. Python has been chosen for the modern code suite for these reasons as well as its expansive collection of modules that can be used for data storage, advanced mathematics, and multidimensional plotting. While translating to a new language is beneficial for widespread use, extensive verification activities must be performed to show code accuracy and to identify any possible errors with either the original or new code. This analysis and error mitigation has been performed and has been documented within past AMA and NASA work⁷.

II.B. Optimization Scheme for Bridging Parameters

In previous iterations of the database, properties below 1000 K were assessed using REFPROP 9.1 while those above 1500 K were calculated using methods similar in approach to those presented here and documented in past McDonald work³. To connect the two datasets and preserve key thermodynamic relationships, a bridging methodology was implemented between 1000 – 1500 K. An internal

Mathcad optimization tool was used to predict the necessary correction factors to the virial state equations as well as enthalpy, entropy, and isobaric specific heat. These parameters are used in every property calculation, thus high accuracy results are required to minimize error at each data point. Prior work derived the parameters at a bridging temperature of 1000 K, or the highest available temperature condition found in the NIST database; however, the correct bridging temperature should correspond to the point where hydrogen dissociation begins to have an impact on the calculated properties. To predict this behavior, the bridging temperature is added as a new parameter with the purpose of driving the ratio of the reaction term of specific heat to the mixture specific heat to a set tolerance value (10^{-8}). The final bridging parameters and boundary constraints are listed in Table II.

TABLE II. Bridging Parameters and Boundary Constraints for the Modern Optimization Routine

Bridging Parameters	Boundary Constraints
Bridging Temperature (BT)	Specific Volume, v
Effective Collision Diameter of H_2 (σ_{H_2})	$\frac{dv}{dP}$
Characteristic Temperature of H_2 (ϵ_{k,H_2})	$\frac{dv}{dT}$
Coefficient for Ideal Gas Law (C_0)	Isobaric Specific Heat, C_p
Coefficient for the First Virial State Term (C_1)	$\left(\frac{C_{p,reaction}}{C_{p,mix}}\right) = 10^{-8}$
Coefficient for the Second Virial State Term (C_2)	Enthalpy, h
Entropy Shift to BT (ΔS_{BT})	Entropy, s

To showcase the impact of the three virial state equation coefficients, the equation of state calculation for specific volume is included in Eq. 1. In this equation, R is the ideal gas law constant, B_{H_2} is the first virial coefficient of dihydrogen, and C_{H_2} is the second virial coefficient of dihydrogen. These two virial coefficients are strongly dependent on the effective collision diameter and characteristic temperature which increases their impact on the specific volume calculation. By varying these five terms, additional smoothing for the specific volume and its partial derivatives between REFPROP and the python calculations is more feasible at the bridging temperature. Application of the entropy shift term effectively removes the implications of the entropy boundary constraint since it serves as a scalar addition to connect REFPROP with the calculated methodology.

$$V_{H_2} = C_0 * \frac{R*T}{P} + C_1 * B_{H_2} + C_2 * \left(\frac{C_{H_2} - B_{H_2}^2}{R*T*P} \right) \quad (1)$$

An in-house minimization routine using a sum of squares error approach was developed in Matlab to determine the best parameters. Other minimization routines and objective functions were investigated, but the extreme nonlinearity of the bridging parameter effects led to rapid divergence within the routine. Utilizing a sum of squares, as shown in Eq. 2, on the residual error creates a smooth multidimensional curve, ϕ , which improves the probability that the optimization sequence will escape local extrema and find global optima.

$$\phi = \min \left[\sum_{i=1}^7 \left(\frac{\text{Python} - \text{REFPROP}}{\text{REFPROP}} \right)^2 \right] \quad (2)$$

Once bridging parameters are identified to match with REFPROP at the converged bridging temperature, the code must connect this new lower temperature bound with the 1500 K lower bound of the high-temperature property calculations. At this 1500 K boundary, all added coefficients (C_0 - C_2) all become unity while the characteristic temperature and collision diameter take on the values reported by Kessel'man which are believed to be the values used to create the Vargaftik reference dataset⁸. To perform this connection, a temperature-dependent cubic weighting function is applied such that each bridging parameter varies smoothly from its converged value at the pressure-informed bridging temperature to the following Kessel'man reported values⁸.

- $\sigma_{H_2} = 2.934 \text{ Angstroms} = 2.934 * 10^{-10} m$
- $\epsilon_{k,H_2} = 34.1 \text{ K}$
- $C_0 = C_1 = C_2 = 1$
- $\Delta S_{BT} = 0$

In addition, the derivative at each temperature end point is set to zero to ensure differentiability of all property functions along the bridging line.

III. VERIFICATION AND VALIDATION

Beyond the extensive verification performed between Mathcad and python following initial translation, additional efforts to compare python results to accepted literature at high temperatures is also required. The legacy datasets that are used in this comparison are the Chemical Equilibrium with Applications (CEA) suite developed by NASA Glenn and the Vargaftik datasets of the ex-Soviet Union. For reference, CEA is the NASA-accepted software for combustion products and fluid properties with dissociation while Vargaftik is the primary dataset upon which the heritage high-temperature SNP parahydrogen properties are based. The National Bureau of Standards (NBS) Monograph 168 for hydrogen properties was also investigated, but this reference dataset sees limited usage

due to a known systemic error in its reported entropy above 2000 K for all pressures considered for the version 05 database.

The primary goal of the validation work is to best match the high-temperature fluid properties with Vargaftik given that the calculations in this legacy document are used within the modern suite. As outlined in the past McDonald work, several editorial errors were identified with the tabulated properties by Vargaftik and have been removed from this validation as well. By direct comparison of results, most temperature-pressure pairs for all properties showed excellent agreement within less than 0.01% error. However, new systematic errors with enthalpy and entropy results have been discovered. For instance, best agreement between the Vargaftik and python methodologies came when removing the unlike interactions terms from the mixture enthalpy calculations and the contributions of the ideal gas terms from the entropy mixture calculation. Neither of these modifications physically represent the contribution of the mixing term from the mixture enthalpy calculation, so it is unknown whether these terms were mistakenly omitted or done so purposefully to avoid the computational effort requirement to yield such small contributions. Given the advancements in modern computational power, these problems are removed, allowing the version 05 database to retain these important physical terms for release.

IV. FINAL DATABASE CAPABILITIES

IV.A. Bridging Parameters

Using the methodology outlined in Section II.B., the final python code is called iteratively within the Matlab-based optimization routine to identify the ideal bridging parameters. Ideal bridging results would create a match to REFPROP within a scaled residual error of less than 10^{-6} . Following convergence, the bridging temperature as a function of pressure can be seen in Fig. 1, and a sampling of the other six bridging parameters versus pressure are shown in Fig. 5. Additionally, residual errors between REFPROP and the python-based calculations for each of the six primary boundary constraints are shown in Fig. 6. Constraining the residual in isobaric specific heat below 10 MPa to 10^{-5} avoids extremely high C_2 values. Without this assumption, the C_2 term exponentially increases which will lead to increased error between the BT and the 1500 K lower bound of the high-temperature property calculations. This assumption still maintains all property errors are still below the accepted tolerance of 10^{-5} . Additionally, C_0 , C_1 , and C_2 are held constant at unity below ~ 188 kPa. This identified optimal value minimizes the error for underlying calculations for entropy and isobaric specific heat.

Trends in the bridging parameters exhibit good behavior between 10 kPa and 100 MPa, so properties below 10 kPa use the bridging parameters at 10 kPa due to ideal gas law assumptions and the minimal error

implications. This assumption has been validated (less than 10^{-8} error for all boundary constraints) below 10 kPa by comparing python values with REFPROP outputs.

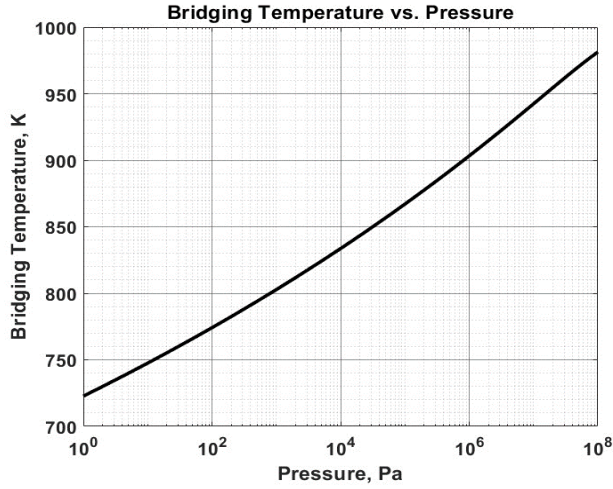


Fig. 1. Converged Bridging Temperature [K] as a Function of Pressure [Pa]

IV.B. Database Creation and Plotting

The primary functionality of the version 05 suite is to create temperature- and pressure-dependent databases based on the preferences of the user. A unique python-based dashboard allows for any temperature and pressure pair as well as arrays of each input to create a 2D matrix of properties. The functionality also allows the user to select any thermophysical or transport property as well as a selection of intermediate calculations to include in the final database. The scheme will call the property functions and calculate each value from the fundamental physics. While this is the highest accuracy approach, it is computationally inefficient for direct calls within a higher fidelity modeling suite. Instead, M&S staff can generate the database to their desired fidelity and create their own interpolation methodology. If this approach is not desired, a pre-built, highly accurate interpolation methodology is included in this suite and is described in Section IV.C.

Additional functionality for multidimensional plotting of each property is also included in the suite. Colored surface or interpolated contour plots depicting the output property values as a function of both temperature and pressure are a sample of the current capabilities. Code modularity easily allows users to add additional python plotting functionality, if desired. Examples of the 3D surface plots for dihydrogen concentration and isobaric specific heat as well as a 2D contour surface plot for viscosity are shown in Fig. 2-4. Residual plotting for the bridging parameters as well as the verification and

validation activities outlined in Section III are also include if needed by the user.

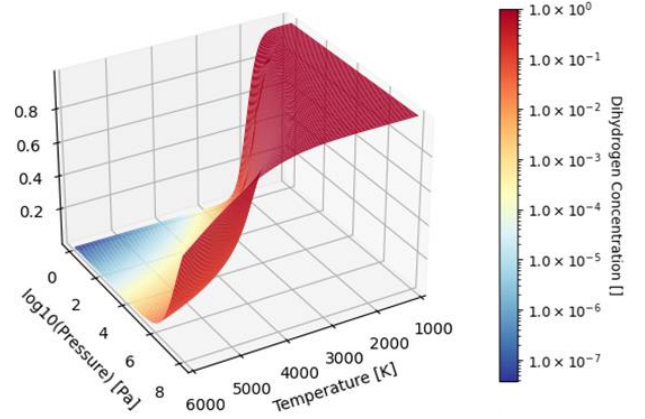


Fig. 2. Dihydrogen Concentration [-] as a Function of Temperature [K] and Logarithmic Pressure [$\log(\text{Pa})$]

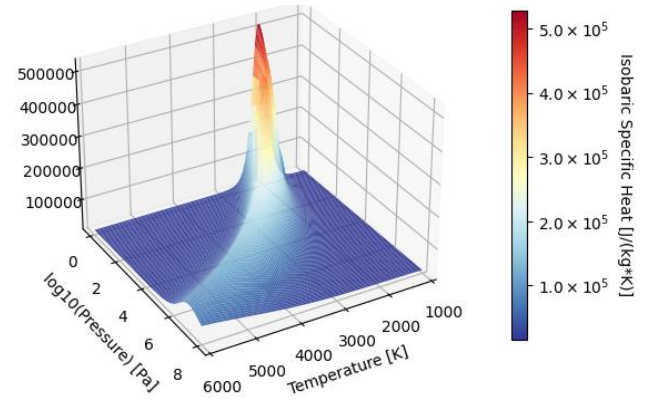


Fig. 3. Isobaric Specific Heat $\left[\frac{\text{J}}{\text{kg}\cdot\text{K}}\right]$ as a Function of Temperature [K] and Logarithmic Pressure [$\log(\text{Pa})$]

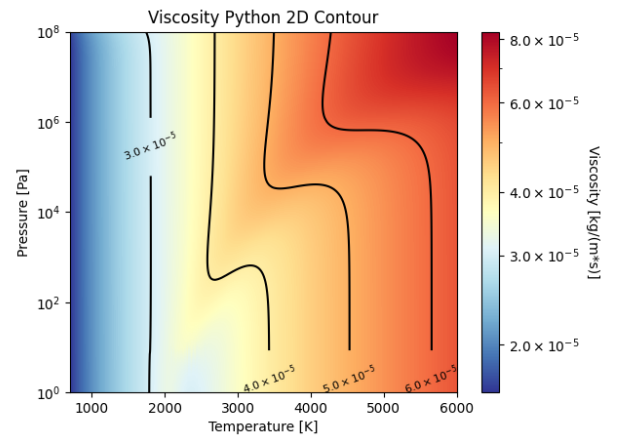


Fig. 4. Dynamic Viscosity $\left[\frac{\text{kg}}{\text{m}\cdot\text{s}}\right]$ as a Function of Temperature [K] and Pressure [Pa]

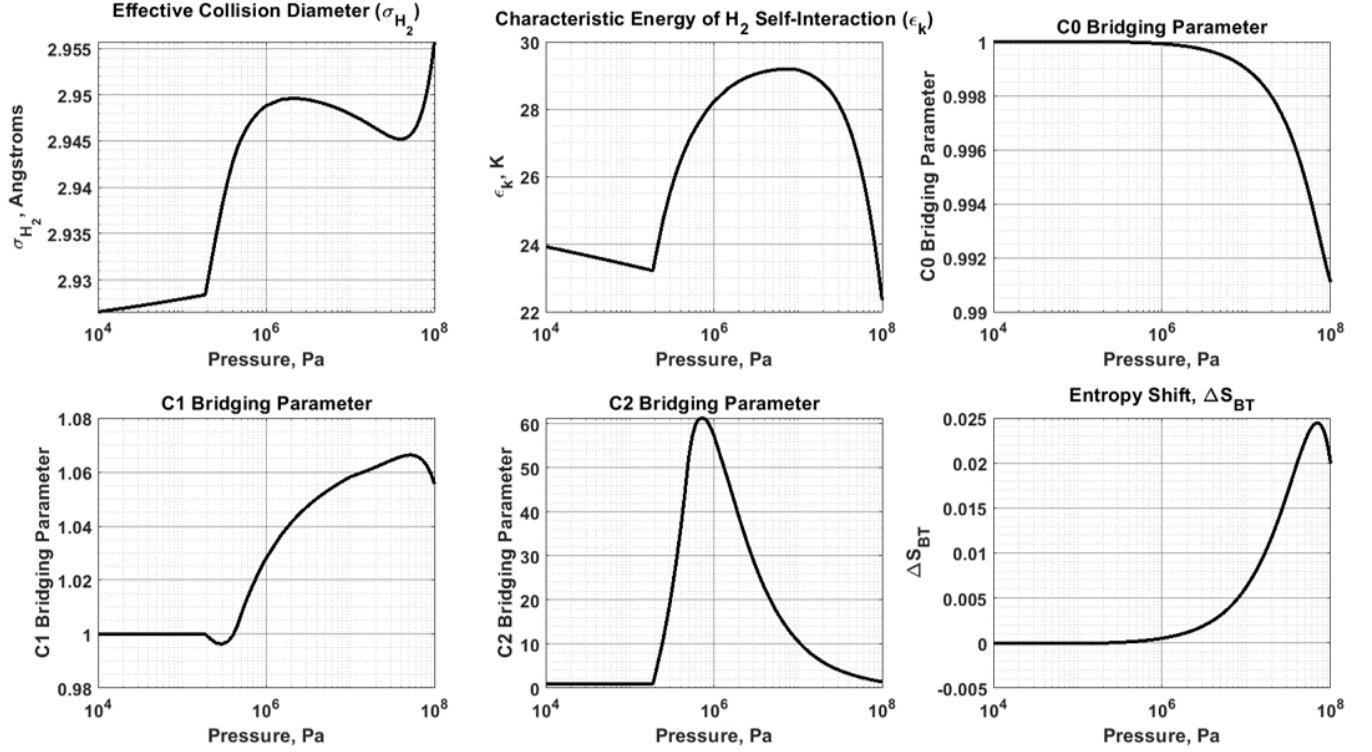


Fig. 5. Converged Bridging Parameters as a Function of Pressure [Pa]

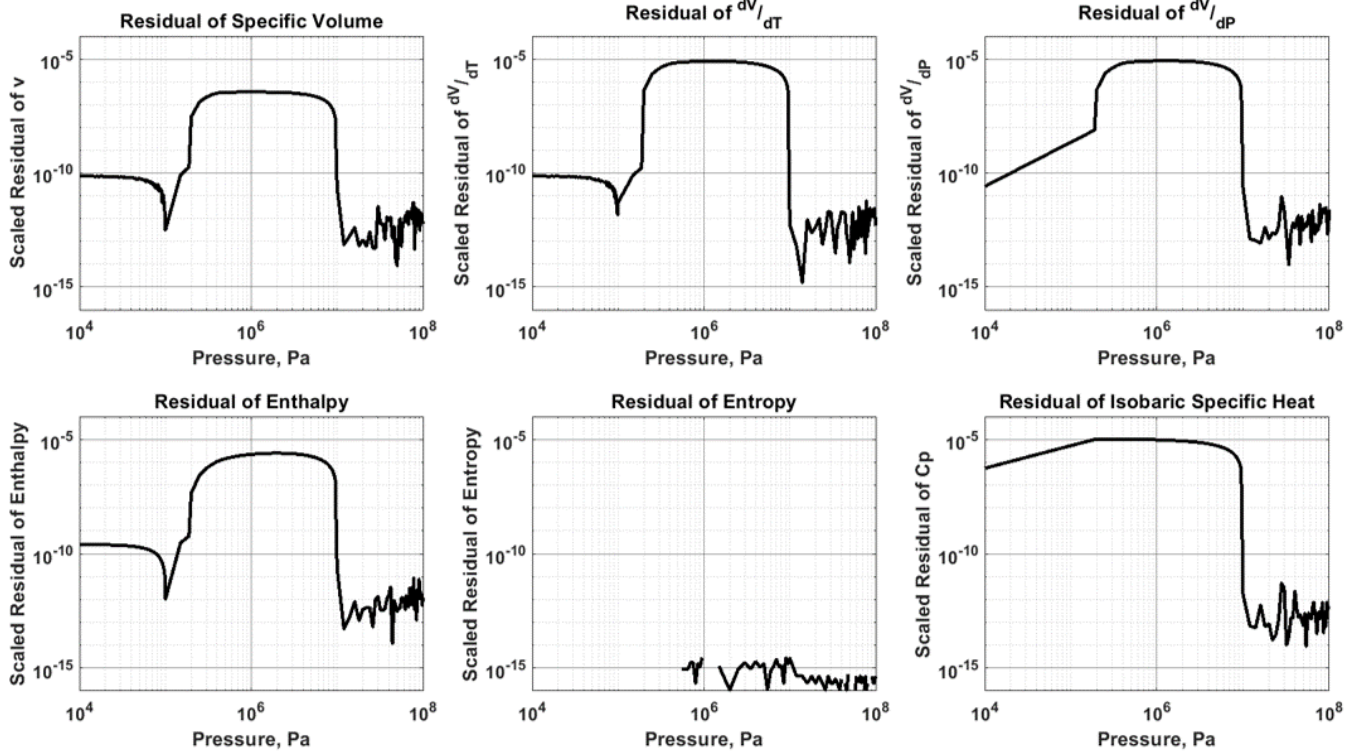


Fig. 6. Boundary Constraint Residual Errors as a Function of Pressure [Pa]

IV.C. On-the-Fly Interpolation

The Python code suite has been used to generate datasets with up to 5 K temperature resolution from 1 Pa to 100 MPa. While these runs are computationally expensive and can take several days, accuracy of the results off of the interpolation “knots”, or input grid values, improves with the finer mesh. Although this project will provide our highest resolution dataset to future users, it may not contain every datapoint that is required. To generate the data for a single pressure and temperature would only take a few minutes, however this is not sustainable for larger temperature and pressure inputs. In order to speed up the calculations for new inputs, an interpolation function was written which uses the existing dataset as a reference.

A Clough-Tocher 2D interpolator from the SciPy interpolate sub-package uses a fast, cubic-based spline that tends to give a smooth interpolating surface which allows local trends to be captured. An added advantage with this interpolator is a rescale input which enables data that differs by many orders of magnitude to be scaled closer to create a better surface. The interpolator functions only need to be generated once for each reference dataset; however, the process only takes 7 seconds if they must be regenerated. Calling the interpolators is even faster; for a vector of 10000 temperatures at one pressure, the script takes approximately 6 seconds for all reference fluid properties. This computation time reduction provides a major benefit to the user while not sacrificing significant accuracy. For the furthest off-the-knot temperatures and pressure combination (2.5 K, 2.5 MPa), the error in xH₂ is zero and the worst performing property, specific volume, yields an error of 0.002% in comparison to the full property calculation.

V. CONCLUSIONS

Modernization of the SNP project’s parahydrogen property database has been focused on upgrades to the high-temperature results by accounting for dissociation. Following external peer review and documentation of key findings, the database has been released to SNP M&S personnel for integration into pre-existing models. Version 05 will become the primary SNP property database given the errors found with version 03b. Intensive verification activities have been performed to showcase the highly accurate results of the new tool. Additionally, advanced capabilities have been added by translating the outdated code framework into a python-based tool that is easily accessible to all industry and government modeling staff supporting both SNP and DARPA DRACO efforts. While dependent on funding and project-level interest, forward work to further modernize the database would be to investigate the chemical and physical effects of cryogenic hydrogen near the saturation dome. Enhancements to the python suite are also possible, such as speed improvements, parallel processing, advanced interpolation

through machine learning and regression, and the usage of different input variables to calculate properties instead of simply pressure and temperature. Efforts are also underway to create a user-friendly API as well as to integrate the property database into INL’s MOOSE framework for higher fidelity finite element analyses.

ACKNOWLEDGMENTS

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