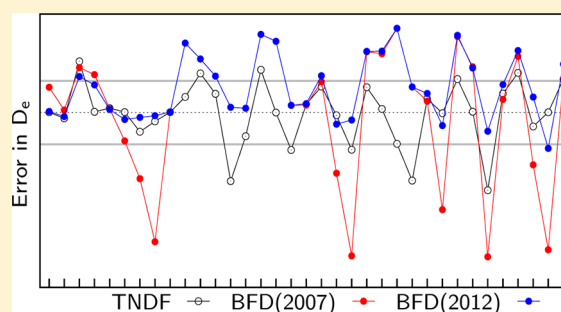


Comparison of Smooth Hartree–Fock Pseudopotentials

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ABSTRACT: The accuracy of two widely used scalar relativistic Hartree–Fock pseudopotentials, the Trail–Needs–Dirac–Fock (TNDF) and the Burkatzki–Filippi–Dolg (BFD) pseudopotentials, is assessed. The performance of the pseudopotentials is tested for a chemically representative set of 34 first-row molecules. All comparisons are made at the Hartree–Fock level of theory, and both sets of pseudopotentials give good results. The all-electron equilibrium geometries, molecular dissociation energies, and zero-point vibrational energies are reproduced a little more accurately by the TNDF pseudopotentials than the BFD ones.



1. INTRODUCTION

Pseudopotentials are used to improve the efficiency of electronic structure calculations by replacing the inert core electrons by an angular momentum-dependent effective core potential. This approach is particularly advantageous for heavy atoms, but it is also useful for light atoms including hydrogen. The use of pseudopotentials is well established within density functional theory (DFT) and Hartree–Fock (HF) theory, and they are also used within correlated quantum chemical methods and in quantum Monte Carlo (QMC) methods.^{1–5} Pseudopotentials can describe the influence of the core electrons on the valence electrons, so that an accurate description of the chemical bonding may be obtained. Near the core, the pseudopotentials, and therefore the accompanying orbitals, are chosen to be as smooth as possible, given the requirement that they reproduce the low-energy electronic states.

In earlier work, we reported the construction of a “periodic table” of smooth pseudopotentials from the Dirac–Fock theory, which we shall refer to as the Trail–Needs–Dirac–Fock (TNDF) pseudopotentials.^{6,7} Another set of smooth HF-based pseudopotentials has been provided by Burkatzki, Filippi, and Dolg (BFD).^{8,9} Both the TNDF and BFD pseudopotentials have been used to calculate the properties of a variety of molecules,^{10–14} clusters,^{15–17} and bulk solids.^{18,19} Pseudopotentials derived within the HF theory are often used in QMC calculations. The smoothness of the pseudopotentials is particularly advantageous for methods using a plane-wave basis and for QMC applications in general. The two sets of pseudopotentials are generated using fundamentally different methods, and it is instructive to compare the accuracy with which they reproduce all-electron (AE) HF results.

Confidence in the application of the TNDF and BFD pseudopotentials, or comparison of their accuracy, requires an assessment of how well they reproduce the properties of a representative set of systems at the AE HF level of theory. All previous assessments and comparisons have been somewhat limited in the physical properties, computational errors, and variety of systems considered. Although the pseudopotentials

may be used for molecules, clusters, and condensed matter systems, it is most convenient to test their performance using small molecules.

In this paper, we evaluate the accuracy with which nonrelativistic HF calculations using the TNDF and BFD pseudopotentials reproduce the molecular geometry, dissociation energy, and zero-point vibrational energy (ZPVE) provided by relativistic AE HF theory. We limit ourselves to the HF theory as both pseudopotential types were constructed to reproduce AE HF results. Similarly, we include relativistic effects in our AE calculations, as both the TNDF and BFD pseudopotentials were constructed to reproduce such effects.

Two comparisons of the TNDF and BFD pseudopotentials have already been reported in the literature.^{8,20} However, for both comparisons, the set of molecules tested was not large enough to draw reliable conclusions, and basis set error was neither estimated nor controlled by using extrapolation methods. In the tests reported here, we have used a larger set of molecules than in the previous tests, and we have carefully studied and largely eliminated the basis set errors.

The test set of molecules was obtained by taking the neutral members of the G1^{21,22} set, removing all molecules that contain atoms other than the series H–F, and adding the H₂, BH, B₂, C₂, and NO₂ molecules, resulting in a test set of 34 molecules. Note that we do not consider Be₂ because it is not bound within HF theory. We include F₂ because restricted HF theory provides a well-defined equilibrium geometry for this molecule even though the dissociation energy takes a physically unrealistic negative value.²³

We confine our attention to the light atoms H–F, which ensures that both the AE and pseudopotential results suffer from negligible basis set error. This allows us to ascribe most of the disagreement between these results to errors in the pseudopotential representation of the core electrons. Separating the basis set and pseudopotential errors is also necessary to

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test the suitability of the TNDF and BFD pseudopotentials for use in diffusion quantum Monte Carlo (DMC) calculations.² Limiting ourselves to these light atoms also ensures that relativistic effects are small, so that the differences due to inconsistent implementations of relativistic effects in the generation of the two pseudopotential types is expected to be small. The goal of our comparison of AE and pseudopotential results is to identify which of the pseudopotential types provides the more accurate reproduction of the AE HF results.

Atomic units are used, unless otherwise indicated, and HF refers to restricted open-shell Hartree–Fock.

2. METHOD

The TNDF pseudopotentials were generated via the construction of pseudoatoms that reproduce the valence contribution to the AE wave function outside of the core region. Inversion of the HF equations then provides an effective potential for each angular momentum channel. The underlying AE states were generated at the Dirac–Fock level of theory, so that the resulting pseudopotential includes the relativistic effects present in the Dirac–Fock theory. This approach is similar to the standard methods used in DFT calculations; however, for the HF theory, the long range of the exchange interaction can lead to a finite value of the pseudopotential at large distances from the core.⁶ This pathological behavior was removed in the generation procedure. Such pseudopotentials are often referred to as “shape consistent”.

The BFD pseudopotentials were generated by taking a Gaussian parametrization of the pseudopotential and determining parameter values that accurately reproduce the AE total energy differences between a number of atomic states. The underlying AE energies were generated at the the Wood–Boring HF level of theory and hence include scalar relativistic effects.²⁴ Such pseudopotentials are often referred to as “energy consistent”.

Both sets of pseudopotentials include relativistic effects and are provided as Gaussian expansions for use in standard quantum chemistry packages. The BFD pseudopotentials do not include the effects of spin–orbit coupling, whereas the TNDF pseudopotentials do. To make the comparisons as fair and useful as possible, we therefore use only the spin-averaged TNDF pseudopotentials, and we do not use the associated spin–orbit potentials.²⁵

In the following, all calculations are performed using the MOLPRO²⁶ quantum chemistry package. All-electron results are obtained using HF theory with the second-order scalar relativistic Douglas–Kroll–Hess Hamiltonian, and therefore, they include scalar relativistic effects but not spin–orbit coupling. Results for both the TNDF and BFD pseudopotentials are generated using nonrelativistic HF theory, and therefore, they include relativistic effects only through the representation of the core electrons by the pseudopotentials. We therefore neglect the very small relativistic effects on the exchange interactions between the valence electrons.

In order to distinguish basis set error from errors due to the pseudopotentials themselves, it is desirable to compare results close to the complete basis set limit and to use the same basis sets for each calculation. We use Dunning basis sets of the aug-cc-pVnZ type in their uncontracted form. Such basis sets provide good convergence properties for both AE and pseudopotential calculations. They also consistently provide lower HF energies than the basis sets provided with the BFD pseudopotentials²⁷ for the first row diatomic molecules.²⁸

A comparison of results close to the complete basis set limit is also appropriate for investigating the accuracy of pseudopotentials for use in diffusion quantum Monte Carlo (DMC) calculations, for which the basis set error is far smaller than that found in HF or quantum chemical calculations.

Optimized geometries, dissociation energies, and ZPVEs are generated for each molecule in our test set. We quantify the dissociation energy as the molecular well depth, D_e , which does not include the ZPVE. Basis set convergence error for each of these quantities is estimated by performing each calculation with two basis sets of the same type but different sizes, indexed by n .

Geometry optimization is performed by direct minimization of the total energy of each molecule for each basis set. To allow the comparison of errors in bond lengths with bond angles and dihedral angles, we map each angle to the arc of a circle of radius 1.0 Å (a typical bond length for the molecules considered). We take the optimum geometry for the largest basis set as our estimate of the equilibrium geometry. We investigate the error in this estimate by extrapolating each geometry parameter to the full basis set limit using the two-point formula

$$x(L) = a + b \exp[-1.335L] \quad (1)$$

where L is the highest angular momentum present in the basis set of index n and taking the difference between the extrapolated value and the estimated values as the estimated error. We do not take the extrapolated limit as our estimate as no error estimate accompanies it and because extrapolation to the complete basis set limit is less reliable for geometries than for total energies.

Note that this formula is the same as that used by Feller²⁹ for three-point extrapolation of optimized geometries of hydrocarbons but with a fixed value of the exponential parameter. This fixed exponential parameter was obtained by considering only the diatomic molecules in the test set. An additional geometry optimization for each of these was performed using the next smallest basis set, allowing three-point extrapolation to be performed with the exponential parameter free to vary. The value of L used in eq 1 is obtained by averaging the resulting exponential parameters over all diatomic molecules in our test set and averaging the parameters arising from both the pseudopotential and AE results.

Well depths, D_e , for each molecule are obtained as the difference between the total energy for each molecule and the sum of the total energies of the component atoms, using consistent basis sets for each. This provides a D_e for each basis set and molecule. Three estimates of the complete basis set limit are provided by the three two-point extrapolation formulas^{31,32}

$$\begin{aligned} D_{e,1}(L) &= a_1 + b_1 L^{-8.74} \\ D_{e,2}(L) &= a_2 + b_2 \exp[-1.95L] \\ D_{e,3}(L) &= a_3 + b_3(L+1) \exp[-9\sqrt{L}], \end{aligned} \quad (2)$$

which may be combined to provide an estimate and error for the complete basis set limit of²⁹

$$D_e = (a_1 + a_2 + a_3)/3 \pm \text{Max}[|a_i - D_e|] \quad (3)$$

Harmonic ZPVEs are obtained within HF theory by diagonalization of the Hessian obtained from numerical energy

Table 1. Deviation of Pseudopotential Results from AE Results^a

	geometry (Å)		D_e (kcal.mol ⁻¹)		ZPVE (kcal mol ⁻¹)	
	MAD	Max	MAD	Max	MAD	Max
TNDF	0.00130	0.00962	0.69457	-2.44325	0.01406	-0.15800
BFD(2012)	0.00230	-0.01332	0.96420	2.65210	0.01989	-0.27500
BFD(2007)	0.00313	-0.01332	1.62093	-4.53708	0.06474	-0.30100

^aPseudopotential errors are summarized in terms of the mean absolute deviation (MAD) of the pseudopotential results from the AE results, and as the maximum deviation (Max) of the pseudopotential results from the AE results (over the test set of molecules). Considering only the TNDF and BFD(2012) data sets, the maximum error for geometry parameters, dissociation energies, and ZPVEs occurs for the B₂, CO₂, and CH₃ molecules described by the BFD(2012) pseudopotentials.

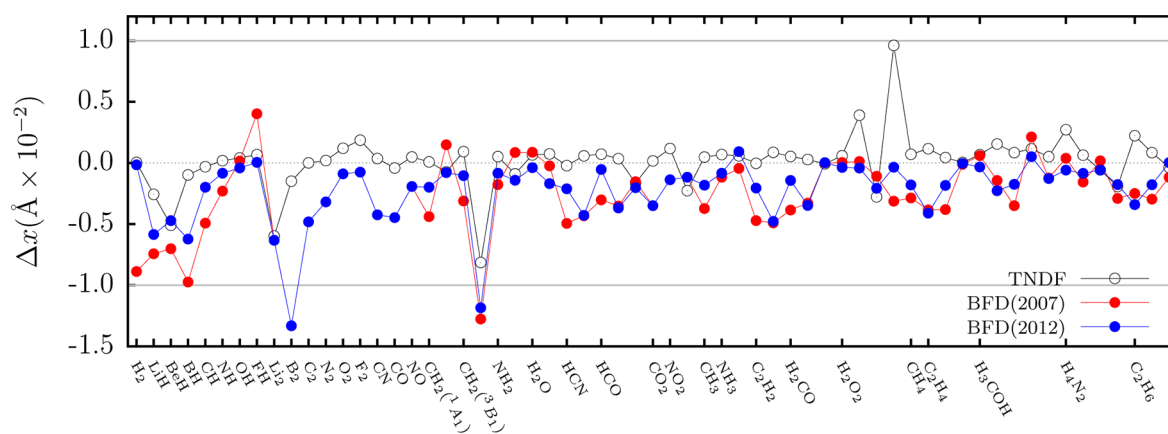


Figure 1. Deviation of the spatial parameters from the AE HF reference data for the TNDF and BFD pseudopotentials. The horizontal gray solid lines at ± 0.01 Å indicate the upper and lower limits of chemical accuracy.

derivatives at the optimum geometry and summation of the contributions from each mode.

Unlike the optimized geometries and D_e , we do not use extrapolation to estimate errors in the ZPVEs because a justification for such an approach is not available in the literature and because the errors in the ZPVEs calculated with a finite basis are small.

We do, however, estimate the basis set error. The estimated ZPVE is taken to be that resulting from the largest basis set used, and the estimated error is taken to be the difference between the ZPVEs resulting from the two basis sets.

Due to finite computational resources and the availability of basis sets, the choice of basis sets is somewhat complex. For all diatomic molecules, we use $n = 5, 6$, except for those containing Li or Be, for which we use $n = 4, 5$. For all other molecules, we use $n = 4, 5$, with the exception of H₂O₂, H₃COH, H₄N₂, and C₂H₆, for which we use $n = 3, 4$. The same pair of basis sets are used for obtaining optimized geometries, well depths, and ZPVEs for all molecules with the exception of C₂H₄, for which we use $n = 4, 5$ for geometry optimizations and well depths and $n = 3, 4$ for ZPVEs.

Since the publication of the original paper of Burkatzki et al.,⁸ a significantly improved BFD pseudopotential for hydrogen has been provided by Filippi and Dolg and used by Petruzielo et al.³⁰ In the following, we present results for both the original set of BFD pseudopotentials, (BFD(2007)), and for the improved H pseudopotential (BFD(2012)). Throughout the text, all discussion and results associated with “BFD pseudopotentials” refers to BFD(2012) unless stated otherwise.

3. RESULTS

First, we consider the basis set errors for our estimated geometries, well depths, and ZPVEs. We found all of these

errors to be well within chemical accuracy of 0.01 Å, 0.57°, and 1 kcal mol⁻¹, with the basis set error (averaged over the AE and pseudopotential results and over the full set of molecules) taking the values 0.0001 Å, 0.0001 kcal mol⁻¹, and 0.004 kcal mol⁻¹ for geometry parameters D_e and ZPVEs, respectively.

For the well depths and ZPVEs, the basis set error is negligible, with peak errors less than 0.06% of chemical accuracy. For the geometry parameters, the error is acceptably small for all molecules, at a few percent of chemical accuracy for most and with a maximum of 15% of chemical accuracy for the dihedral angle of H₂O₂.

Our goal is to assess the accuracy with which the pseudopotentials reproduce the AE results; hence, we take our AE results as the baseline and consider only the deviation of the pseudopotential results from this baseline. Because this is a difference between calculated quantities, basis set error is further reduced by correlations between the errors present in the AE and pseudopotential results.

The basis set error in the difference between our pseudopotential and AE well depths and ZPVEs remains negligible, and the error in the differences for geometry parameters is not significant with a mean basis set error of 0.0001 Å for geometry differences.

We summarize the pseudopotential error over the test set in terms of the mean absolute deviation (MAD) of the pseudopotential results from the AE results and the maximum absolute deviation of the pseudopotential results from the AE results. The data are provided in Table 1.

3.1. Optimized Geometries. Figure 1 shows the errors in the optimum geometry parameters for the two pseudopotential types. Overall, the TNDF pseudopotentials reproduce the AE geometries more accurately than the BFD ones, with a few exceptions. The MAD (with respect to the AE results) arising

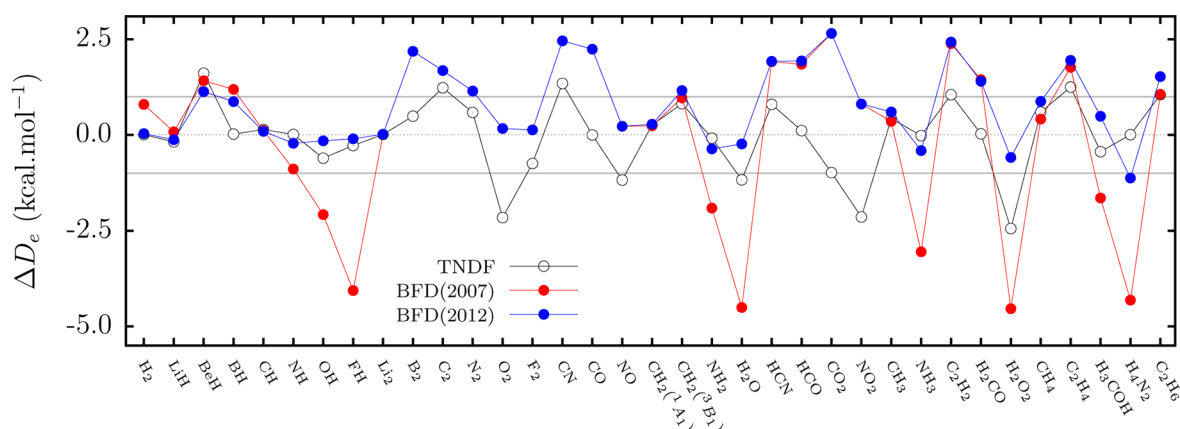


Figure 2. Deviation of the well depths from the AE HF reference data for the TNDF and BFD pseudopotentials. The horizontal gray solid lines at ± 1 kcal mol $^{-1}$ indicate the upper and lower limits of chemical accuracy. The estimated basis set error is negligible on the scale of the figure.

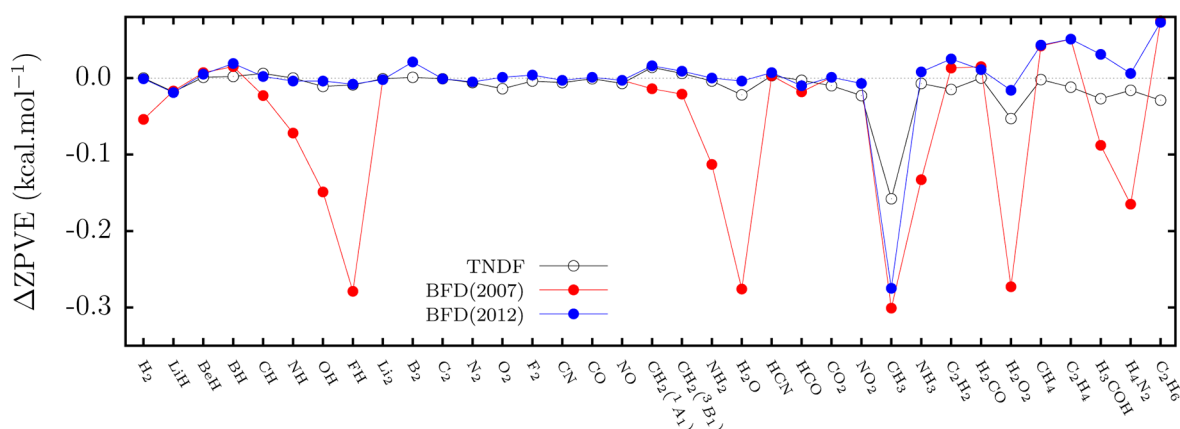


Figure 3. Deviation of the ZPVEs from the baseline AE HF reference data for the TNDF and BFD pseudopotentials.

with the BFD pseudopotentials is 1.8 times greater than that for the TNDF pseudopotentials. There is a trend for the BFD pseudopotentials to underestimate bond lengths, with geometry parameters showing an average deviation from the AE results of -0.002 Å, whereas for the TNDF pseudopotentials the average deviation is only 0.0001 Å. Unlike the BFD pseudopotentials, all of the geometries obtained with the TNDF pseudopotentials fall within chemical accuracy of the AE geometries.

The geometry of H_2O_2 stands out as the worst case for the TNDF pseudopotentials, with a significantly larger error than the equivalent result with BFD pseudopotentials. We have not found an explanation for this difference, but we note that the shallow variation of the total energy with geometry for this molecule is known to result in an optimum geometry that is unusually sensitive to errors in the total energy.

3.2. Well Depths. Figure 2 shows the errors in well depths at optimum geometries for the two pseudopotential types. Overall the TNDF pseudopotentials reproduce the AE D_e values more accurately than the BFD pseudopotentials, with error in well depths for the TNDF pseudopotentials smaller than that for the BFD pseudopotentials for 24 out of the 34 molecules studied. In summary, the MAD (with respect to the AE results) for the BFD pseudopotentials is 1.4 times greater than that for the TNDF pseudopotentials. The BFD pseudopotentials tend to overestimate D_e , with an average deviation from AE values of 0.78 kcal mol $^{-1}$, whereas for the TNDF pseudopotentials the average deviation is -0.015 kcal mol $^{-1}$.

Figure 2 also shows the errors in well depth that arise with the original BFD hydrogen pseudopotential (BFD(2007)). The poor performance of the original hydrogen pseudopotential is most apparent for molecules containing H bonded to N, O, or F, the most electronegative atoms considered. On examination of the updated pseudopotentials, it is clear that the poor transferability of the original BFD pseudopotential can be ascribed to it deviating from the Coulomb potential over a core region that is too large.

3.3. Harmonic Zero-Point Vibrational Energies. Figure 3 shows the errors in the ZPVEs for the two pseudopotential types. Overall, the TNDF pseudopotentials reproduce the AE ZPVEs more accurately than the BFD pseudopotentials; the MAD (with respect to the AE results) for the BFD pseudopotentials is 1.4 times greater than that for the TNDF pseudopotentials. However, the errors themselves are considerably smaller than chemical accuracy and both pseudopotential types can be considered as chemically accurate for ZPVEs.

Figure 3 also clearly shows that for the original BFD hydrogen pseudopotential (BFD(2007)) the errors in the ZPVEs are dominated by the poor description of H bonding with N, O, or F. The data also demonstrates that the updated BFD hydrogen pseudopotential removes most of this error, with a large reduction in the error associated with a few molecules reducing the BFD MAD by a factor of $0.31 \times$.

4. CONCLUSIONS

Due to the large test set used, our comparison of the performance of the TNDF and BFD pseudopotentials at the HF level of theory is more reliable than those of previous authors. Because the pseudopotentials themselves are constructed to reproduce AE HF results, performing our analysis using the HF theory does not limit the validity of our conclusions. We believe that the accuracy comparison provided here is more complete than those of previous authors.^{8,20} We have explicitly controlled the basis set error, have considered optimum geometries and ZPVEs as well as dissociation energies, and have considered a larger set of molecules chosen to be representative of the chemical properties of the first row atoms.

For the large test set of molecules considered, the TNDF pseudopotentials reproduce (relativistic) AE results for optimized geometries, well depths, and ZPVEs to a modestly higher accuracy than the BFD pseudopotentials. The MADs of the pseudopotentials results from the AE results are 1.8, 1.4, and 1.4 times greater for the BFD pseudopotentials than for the TNDF pseudopotentials for geometry parameters, well depths, and ZPVEs, respectively. The main limitation of this study is that only first row atoms have been considered, and it would be premature to draw conclusions about the performance of the two pseudopotential types for heavier atoms.

Overall, the small improvement of the TNDF over the BFD pseudopotentials is most significant for optimized geometries and dissociation energies. The calculated ZPVEs are well within chemical accuracy.

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Notes

The authors declare no competing financial interest.

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