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Automatic Differentiation in Quantum Chemistry with Applications to Fully Variational Hartree−Fock

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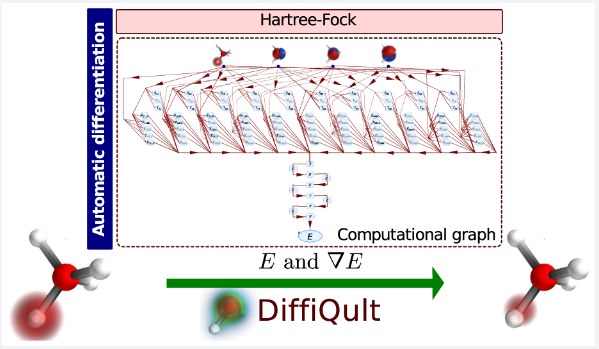
Supporting Information

ABSTRACT: Automatic differentiation (AD) is a powerful tool that allows calculating derivatives of implemented algorithms with respect to all of their parameters up to machine precision, without the need to explicitly add any additional functions. Thus, AD has great potential in quantum chemistry, where gradients are omnipresent but also difficult to obtain, and researchers typically spend a considerable amount of time finding suitable analytical forms when implementing derivatives. Here, we demonstrate that AD can be used to compute gradients with respect to any parameter throughout a complete quantum chemistry method. We present *DiffiQult*, a Hartree−Fock implementation, entirely differentiated with the use of AD tools. *DiffiQult* is a software package written in plain Python with minimal deviation from standard code which illustrates the capability of AD to save human effort and time in implementations of exact gradients in quantum chemistry. We leverage the obtained gradients to optimize the parameters of one-particle basis sets in the context of the floating Gaussian framework.



1. INTRODUCTION

Automatic differentiation (AD) is a conceptually well-established tool to calculate numerical gradients up to machine precision,[1,2] by iteratively applying the chain rule and successively walking through the computational graph of numerically implemented functions. Therefore, AD facilitates the computation of exact derivatives of coded algorithms with respect to all its variables without having to implement any other expression explicitly. AD circumvents challenges arising in traditional approaches. For example, the evaluation of analytical expressions tends to be inefficient, and numerical gradients can be unstable due to truncations or round-off errors. Enabled by a variety of libraries,[3−11] AD has been successfully implemented to various applications.[12−14] For example, AD has been used for quantum control in open-quantum systems to find an optimal time-dependent field to obtain a specific state.[15,16] Furthermore, new libraries developed in the context of deep learning[9,17−19] make AD techniques even more accessible to a broader community. For instance, Leung et. al used a parallelized machine learning tool, TensorFlow, to obtain the optimal parameters to minimize several kinds of cost-functions to tune the evolution of quantum states.[20]

In this manuscript, we highlight the relevance of AD for quantum chemistry and demonstrate that AD provides a novel general path forward to reduce the human time spent on the implementation gradients for electronic structure methods. Gradients play a fundamental role in optimization procedures as well as for the computation of molecular response properties such as dipole moments polarizabilities, magnetizabilities, or force constants.[21] Although analytical expressions are available for some derivatives in many cases,[22−25] researchers typically spend a considerable amount of time finding suitable analytical forms when implementing new quantum chemistry methods.[18] Depending on the complexity of the electronic structure method, this can result in a significant time delay between the development of the method and the implementation of its gradients. The implementation of geometrical gradients for MC-SCF[21,26] has been published more than 10 years after the method itself.[27] Moreover, some analytical gradients can be too complicated to be handled manually. For example, the complex analytical derivatives of the FIC-CASPT2[28,29] method, published more than two decades ago, has been only recently accessible through advances in automatic code generation.[30,31]

AD techniques could play an important role in quantum chemistry by marginalizing the complexity of implementing gradients, as it allows computing the gradients without coding

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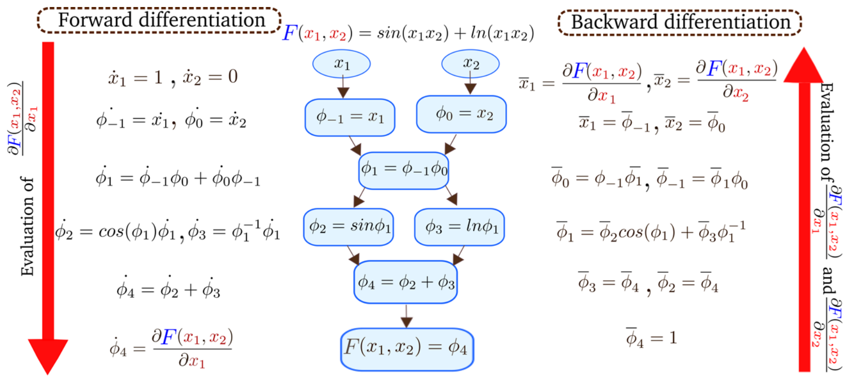
Forward differentiation
$F(x_1, x_2) = sin(x_1x_2) + ln(x_1x_2)$
Backward differentiation
Evaluation of $\frac{\partial F(x_1,x_2)}{\partial x_1}$
$\dot{x}_1 = 1$, $\dot{x}_2 = 0$
$\dot{\phi}_{-1} = \dot{x}_1$, $\dot{\phi}_0 = \dot{x}_2$
$\dot{\phi}_1 = \dot{\phi}_{-1}\phi_0 + \dot{\phi}_0\phi_{-1}$
$\dot{\phi}_2 = cos(\phi_1)\dot{\phi}_1$, $\dot{\phi}_3 = \phi_1^{-1}\dot{\phi}_1$
$\dot{\phi}_4 = \dot{\phi}_2 + \dot{\phi}_3$
$\dot{\phi}_4 = \frac{\partial F(x_1,x_2)}{\partial x_1}$
x_1
x_2
$\phi_{-1} = x_1$
$\phi_0 = x_2$
$\phi_1 = \phi_{-1}\phi_0$
$\phi_2 = sin\phi_1$
$\phi_3 = ln\phi_1$
$\phi_4 = \phi_2 + \phi_3$
$F(x_1, x_2) = \phi_4$
$\bar{x}_1 = \frac{\partial F(x_1,x_2)}{\partial x_1}$, $\bar{x}_2 = \frac{\partial F(x_1,x_2)}{\partial x_2}$
$\bar{x}_1 = \bar{\phi}_{-1}$, $\bar{x}_2 = \bar{\phi}_0$
$\bar{\phi}_0 = \phi_{-1}\bar{\phi}_1$, $\bar{\phi}_{-1} = \bar{\phi}_1\phi_0$
$\bar{\phi}_1 = \bar{\phi}_2 cos(\phi_1) + \bar{\phi}_3\phi_1^{-1}$
$\bar{\phi}_3 = \bar{\phi}_4$, $\bar{\phi}_2 = \bar{\phi}_4$
$\bar{\phi}_4 = 1$
Evaluation of $\frac{\partial F(x_1,x_2)}{\partial x_1}$ and $\frac{\partial F(x_1,x_2)}{\partial x_2}$

Figure 1. The center depicts the computational graph of a simple function $F(x_1, x_2)$ and its elementary operations. On the left and right, we illustrate the differentiation steps of forward and backward mode, respectively. In forward mode, the evaluation of the function at a given set of parameter and the derivative with respect to x_1 is evaluated by computing the intermediate variables ϕ_i and their derivatives following the order of the computational graph using the chain rule. The direction of the evaluation is indicated by the left arrow. In backward mode, the function is evaluated first at a given value, and later the adjoints of all the intermediate variables are computed by iterating backward through the computational graph, indicated by the right arrow. Notice, in this mode, the partial derivatives of the function with respect to the two independent variables are computed together, whereas in forward mode each partial derivative of the function has to be evaluated separately. In this example, to compute the entire gradient, the number of operations in backward mode is smaller than in forward mode.

them explicitly. The advantages of AD techniques have been used before in electronic structure methods.[32−36] In these previous works, the implementations were tailored to the differentiation of the specific application. These typically require considerable changes to existing code or the explicit implementation of some analytical gradients, Taylor coefficients, or adjoints. For instance, in the context of density functional theory, a combined approach using analytical expression together with AD has been successfully applied to compute higher order derivatives of the exchange-correlation term.[32] Further, Sorella et al.[36] explicitly derived the appropriate sequence of computation of adjoints and their expressions for the kinetic and potential energy terms. Here, we apply AD in a broader context and demonstrate that AD tools are an efficient way to get arbitrary gradients for a complete quantum chemistry method with respect to any input parameter. To this end, we implement a fully autodifferentiable Hartree−Fock (HF) method which we distribute in our *DiffiQult* software package[37] written in plain Python language. We have selected HF since it is not only used in many electronic correlation methods as an initial step but contains complex mathematical operations and functions, such as calculating derivatives of eigenvectors or special functions. The latter is also relevant for more sophisticated quantum chemistry methods[38] and impose nontrivial requirements for suitable AD libraries as they need to lay out the complete computational graph rather than calling black-box routines, for example, implemented in LAPACK.[39] We illustrate the capabilities of *DiffiQult* within the framework of a fully variational HF method, where we use a gradient-based optimization of the SCF-energy to optimize the parameters of the basis set within the Floating Gaussian framework.[40,41] Our implementation sets the basis for extending the *DiffiQult* software package to include post-HF methods such as FCI and MP2, and to leverage higher order derivatives to obtain anharmonic corrections for rotational−vibrational spectroscopy.

This paper is organized as follows: In section 2, we provide a small review of the algebra behind automatic differentiation. In the section 3 we introduce the fully variational Hartree−Fock method. In section 4, we discuss in detail the key components of the canonical HF algorithm and explain how they were implemented in *DiffiQult* by considering an appropriate selection and usage of an AD library. In Section 5 we demonstrate the capabilities of our algorithm by optimizing the one-electron basis functions of small molecules. Finally, in section 6, we conclude with an outlook of future directions of *DiffiQult*, and a perspective of the role of AD in simplifying and accelerating the implementation of gradients of new quantum chemistry methods.

2. AUTOMATIC DIFFERENTIATION

The idea behind automatic differentiation is that every algorithm, independent of its complexity, consists of a series of simple arithmetic operations that have known analytical forms, such as sums, multiplications, sines, cosines, or exponents. The sequence of these elementary operations is represented by a computational graph; see for example Figure 1. In this form, it is possible to compute the gradients of the outputs of a function with respect to its inputs by applying the chain rule and evaluating the analytical derivatives of all of these elementary operations in a given order. This implies that AD libraries can differentiate the entire algorithm not only mathematical expressions, written in an explicit form, but also all the control functions such as recursions, loops, conditional statements, etc. Therefore, AD computes the exact derivatives of any code with machine precision.[1] In practice, there are two main forms to compute derivatives using the chain rule with AD tools: forward and backward mode. We illustrate both modes in Figure 1.

Forward mode is conceptually the easiest way to compute gradients. Let us consider the function F: $\mathcal{R}^n \rightarrow \mathcal{R}^m$ defined by a sequence of k functions, f_i: $\mathcal{R}^{n_i} \rightarrow \mathcal{R}^{n_{i+1}}$ in the following way $y = F(x) = (f_k{}^\circ f_{k-1}{}^\circ..f_1{}^\circ f_0)(x)$. In forward mode, the partial derivative of a function with respect to a given parameter x_j, $\dot{y} = \frac{\partial y}{\partial x_j}$, is computed by evaluating simultaneously the intermediate variables $\phi_{i+1} = f_i(\phi_i)$ and the derivatives $\dot{\phi}_{i+1} = \frac{\partial f_i}{\partial \phi_i}(\phi_i)\dot{\phi}_i$, at a given $x = a$. Note that $\phi_0 = x$ and $\dot{\phi}_0 = \dot{x} = \frac{\partial x}{\partial x_j}$. Once we defined the values of the independent variables, the algorithm proceeds to calculate ϕ_1 and $\dot{\phi}_1$, and will continue to compute the partial derivatives of the next elementary operations following the computational graph by sequentially applying the chain rule. For instance, the differentiation of a function F with a single dependent variable goes from right side to left side of the equation,

$$\begin{aligned}\dot{y} &= \left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_a = \frac{\mathrm{d}y}{\mathrm{d}\phi_k}\left(\frac{\mathrm{d}\phi_k}{\mathrm{d}\phi_{k-1}}\cdots\left(\frac{\mathrm{d}\phi_1}{\mathrm{d}\phi_0}\left(\frac{\mathrm{d}\phi_0}{\mathrm{d}x}\right)\right)\right)\\ &= \frac{\mathrm{d}y}{\mathrm{d}\phi_k}\left(\frac{\mathrm{d}\phi_k}{\mathrm{d}\phi_{k-1}}\cdots\left(\frac{\mathrm{d}\phi_1}{\mathrm{d}\phi_0}(\dot{\phi}_0(x))\right)\right)\\ &= \frac{\mathrm{d}y_i}{\mathrm{d}\phi_k}\left(\frac{\mathrm{d}\phi_k}{\mathrm{d}\phi_{k-1}}\cdots(\dot{\phi}_2(\phi_1))\right)\end{aligned} \tag{1}$$

An example of forward differentiation of a more complex function with two variables is illustrated on the left side in Figure 1. We display the steps to compute the partial derivatives of the intermediate variables with respect to a single parameter. Since the forward mode relies on the generation of the derivatives of the elementary operations with respect to each individual input parameter, it is particularly suited for functions with few independent variables.

The second form is backward mode, which relies on the computation of the "adjoints" $\bar{x} = \frac{\partial F^T}{\partial x_j}\bar{y}$ by computing the adjoints of the intermediate variables, $\bar{\phi}_i = \left[\frac{\partial f_i}{\partial \phi_i}(\phi_i)\right]^T \bar{\phi}_{i+1}$. In contrast to forward mode, in backward mode the adjoints are computed following the opposite direction through the computational graph by iterating computing each adjoint of all the intermediate variables. The algorithm first evaluates the function $F(x)$ at a given set of parameters $x = a$, and later proceeds to calculate the adjoints of the last intermediate variable to the first one iterating backward through the computational graph. By definition, $\phi_k = y$, therefore $\bar{\phi}_k = 1$. If $F(x)$ only depends on a single parameter, this procedure is the equivalent of evaluating the chain rule from left to right,

$$\begin{aligned}\bar{x} &= \left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{\mathbf{a}} = \frac{\mathrm{d}F^T}{\mathrm{d}x}\bar{y} = \left(\left(\left(\left(\frac{\mathrm{d}y}{\mathrm{d}\phi_k}\right)\frac{\mathrm{d}\phi_k}{\mathrm{d}\phi_{k-1}}\right)\cdots\frac{\mathrm{d}\phi_1}{\mathrm{d}\phi_0}\right)\frac{\mathrm{d}\phi_0}{\mathrm{d}x}\right)\\ &= \left(\left(\left((\bar{y}(\phi_k))\frac{\mathrm{d}\phi_k}{\mathrm{d}\phi_{k-1}}\right)\cdots\frac{\mathrm{d}\phi_1}{\mathrm{d}\phi_0}\right)\frac{\mathrm{d}\phi_0}{\mathrm{d}x}\right)\\ &= \left(\left((\bar{\phi}_k(\phi_{k-1}))\cdots\frac{\partial\phi_2}{\partial\phi_1}\right)\frac{\partial\phi_1}{\partial x}\right).\end{aligned} \tag{2}$$

The last step of backward mode, after calculating all the intermediate adjoints, results in the partial derivatives of the function with respect to all parameters. An example with a more complex composition of function with two variables is illustrated on the right side of Figure 1, where we get the entire gradient of $F(x_1, x_2)$ with a single backward propagation evaluation. Note that intermediate adjoints can be used at a later stage to obtain the partial derivatives with respect to both variables resulting in a reduction of operations compared to the forward differentiation. This characteristic generally makes the backward mode more efficient for a small number of dependent variables. For more details about the general differences over both modes and its implementation, the reader might refer to ref 2.

In practical applications, the choice of either differentiation mode depends on the specific form of the computational graph as well as on performance considerations taking into account the available computational resources. For example, backward mode requires either storing the complete sequence of operations of the algorithm to compute the function or recalculating the intermediate variables. On the other hand, this constraint might be compensated by the capability of the backward mode to efficiently evaluate derivatives of many parameters with fewer operations than the forward mode. In our particular case, this analysis is done by reviewing the relevant mathematical operations of a canonical HF algorithm for an efficient implementation of gradients with AD techniques.

3. FULLY VARIATIONAL HARTREE–FOCK

Our goal is to implement gradients with AD techniques for a quantum chemistry method without writing any explicit gradient. In this manuscript, as an illustrative, yet useful example, we apply AD to obtain HF energy gradients to optimize parameters of Gaussian basis functions. This algorithm will enable a more compact wave function representation while maintaining a comparable level of accuracy in energy achieved by using larger basis sets. Thus, this method will provide tailored molecular one-electron basis functions with greater flexibility compared to atomic-centered Gaussian expansions.

In the HF method, the wave function is constructed as a linear combination of one-electron basis functions, where we minimize the energy by finding the appropriate expansion coefficients. The selection of these basis functions is critical to accurately reproduce the behavior of a system.[42] The most popular form of these basis functions is the atomic-centered contracted Gaussian functions because the computation of one- and two-electron integrals have well-established forms for their implementations.[24,43−45] Each of these functions is defined by the set of following parameters: (i) the exponents $\{\alpha\}$ defining the Gaussian width, (ii) the contraction coefficients $\{c\}$ defining the linear expansion of the Gaussian representation of the atomic orbital (AO), (iii) the coordinates $\mathbf{A}$ defining the center of the Gaussians, and (iv) the angular momentum $\mathbf{a}$ defining the order of the polynomial factor defined by the coordinate system (e.g., Cartesian or spherical harmonics).[46]

These one-electron basis functions are generally obtained by energy optimizations of single atoms with a certain level of theory and are intended to mimic AO.[47] However, when AOs are used as a basis for molecules they require some degree of flexibility to describe more complex behaviors such as polarization effects. Therefore, one usually selects a relatively large number of basis functions with AOs of different exponents and sufficiently high angular momentum.[42] The drawback of using a larger basis set is the increase in numerical complexity, imposing limitations on actual calculations.

To get a fully optimized wave function, we can minimize not only the expansion coefficients, but all types of variational parameters of the Gaussian AOs mentioned above, such as nuclear coordinates, Gaussian centers, contraction coefficients, and exponents. A fully variational approach may be useful to reduce the number of basis functions and to obtain a more compact representation of the wave function. This could either improve the calculation of molecular properties[40,42,48] or yield a better reference state for certain higher levels of theory.[49] A prominent example of a variational approach is the so-called Floating Gaussians[41,50−52] in which the centers of the AOs are optimized. Some authors have partially optimized parameters such as the Gaussian widths for the valence shell[40] or included extra orbitals around the region of the chemical bond.[53,54] Furthermore, wave function parameters have been optimized within a higher level of theory,[55,56] such as CASSCF and MP2,[57] or HF over ab initio molecular dynamics.[58,59] These methods have implemented gradient or Hessian-based optimization with analytical nuclear derivatives.

In this paper, we present a fully variational approach,[56] where we optimize the molecular orbitals with a quasi-Newton method. Here, the gradients are calculated using solely a plain Python implementation of a HF and an AD library. By taking advantage of the AD techniques, we can compute numerically exact gradients with respect to any parameter without the need for implementing analytical gradients explicitly. This provides the flexibility to either simultaneously optimize the Gaussian exponents and positions, or to optimize them sequentially.

4. IMPLEMENTATION

In the following section, we describe *DiffiQult*, a fully variational HF algorithm that calculates gradients employing AD. In particular, we discuss options and constraints that need to be considered when applying AD in a quantum chemistry method. *DiffiQult* contains two main parts, (i) a restricted HF implementation that provides HF energies as well as its derivatives with respect to any input parameter and (ii) a gradient-based optimization of wave function parameters. The scheme of our fully variational Hartree−Fock implementation is shown in Figure 2.

The philosophy behind using AD is centered around the idea of saving human effort in the implementation of gradients. Ideally, we would like to choose a suitable AD library capable of getting gradients from AD just by adding minimal changes to standard Python or C++ code. In this way, we would be able to significantly reduce the amount of time required for the implementation of gradients for new electronic structure methods. Moreover, we could link the AD library to existing electronic structure software packages for which analytical or numerical gradients might be inefficient. However, to what extent the aforementioned goals can be reached depends on the capabilities of the available AD libraries.[3,4,60−63] Each of the libraries differs in some aspects, but all of them have in common that they are restricted in some way, and it remains to be analyzed which ones match the requirements for a quantum chemistry algorithm best. For example, we would need to differentiate some operations that are typically computed by library routines, e.g., LAPACK[39] functions. To avoid explicit implementation of those methods, an appropriate library preferably supports linear algebra operations as well as calls to special functions such as the incomplete gamma function. Similarly, the AD modes, e.g., forward or backward mode, as discussed in section 2 exhibit different properties, and one might be more suitable for a particular implementation than the other. A majority of the requirements are shared among various electronic structure algorithms, including HF. Therefore, the gradients computed solely with AD techniques of a HF implementation in *DiffiQult* serves as a proof-of-concept that

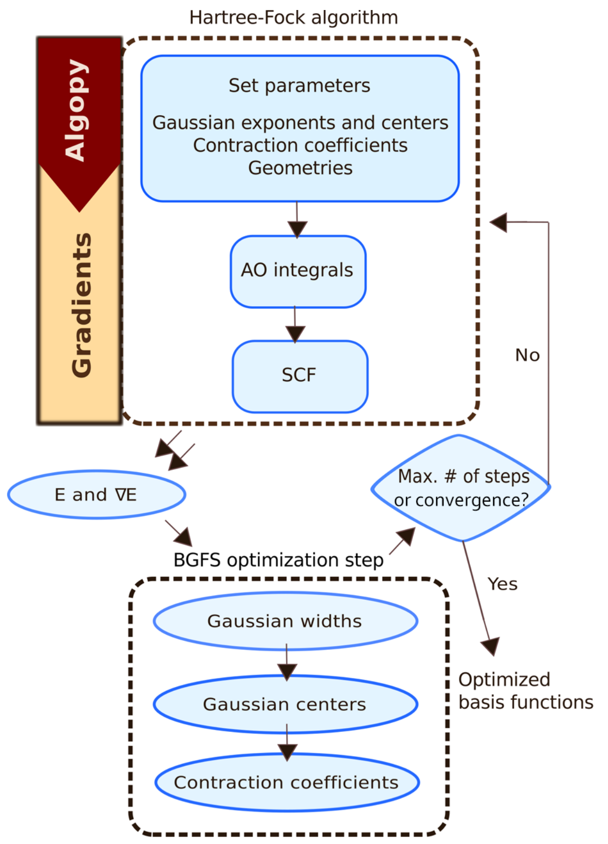

Figure 2. Diagram of the fully variational algorithm implemented in the *DiffiQult* package.

helps us to develop an understanding of the capabilities of AD in quantum chemistry.

In the following analysis, we review how the library and AD mode selection impact the implementation of *DiffiQult*. We should notice that certain operations that are simple in standard implementations can raise challenges depending on the selected AD library. For example, some control flow statements that depend on intermediate variables might impose some constraints in backward mode, if the library builds the computational graph before the evaluation of the function. In HF, control statements are for example implemented to determine the required number of SCF steps for convergence. Depending on the input parameter, e.g., the molecular geometry, fewer or more iterations are needed to reach convergence, and thus the computational graph consists of fewer or more operations. This has severe implications on the backward mode since for this mode the computational graph needs to be fixed before function evaluation. We might circumvent some of these issues by hard-coding the number of steps of the SCF, but this simple example demonstrates that the implementation of gradients with AD tools requires different considerations when compared to developing traditional software packages.

Another relevant aspect for the implementation of *DiffiQult* is the matrix operations. From the algorithmic point of view, we should leverage vectorized operations whenever possible.[64] Vectorized operations are taken as elementary operations in most of the AD libraries, and the computation of their derivatives is typically stated in a simple vectorized form which avoids unnecessary storage and evaluations of intermediate variables. However, in HF, as essentially in all wave function

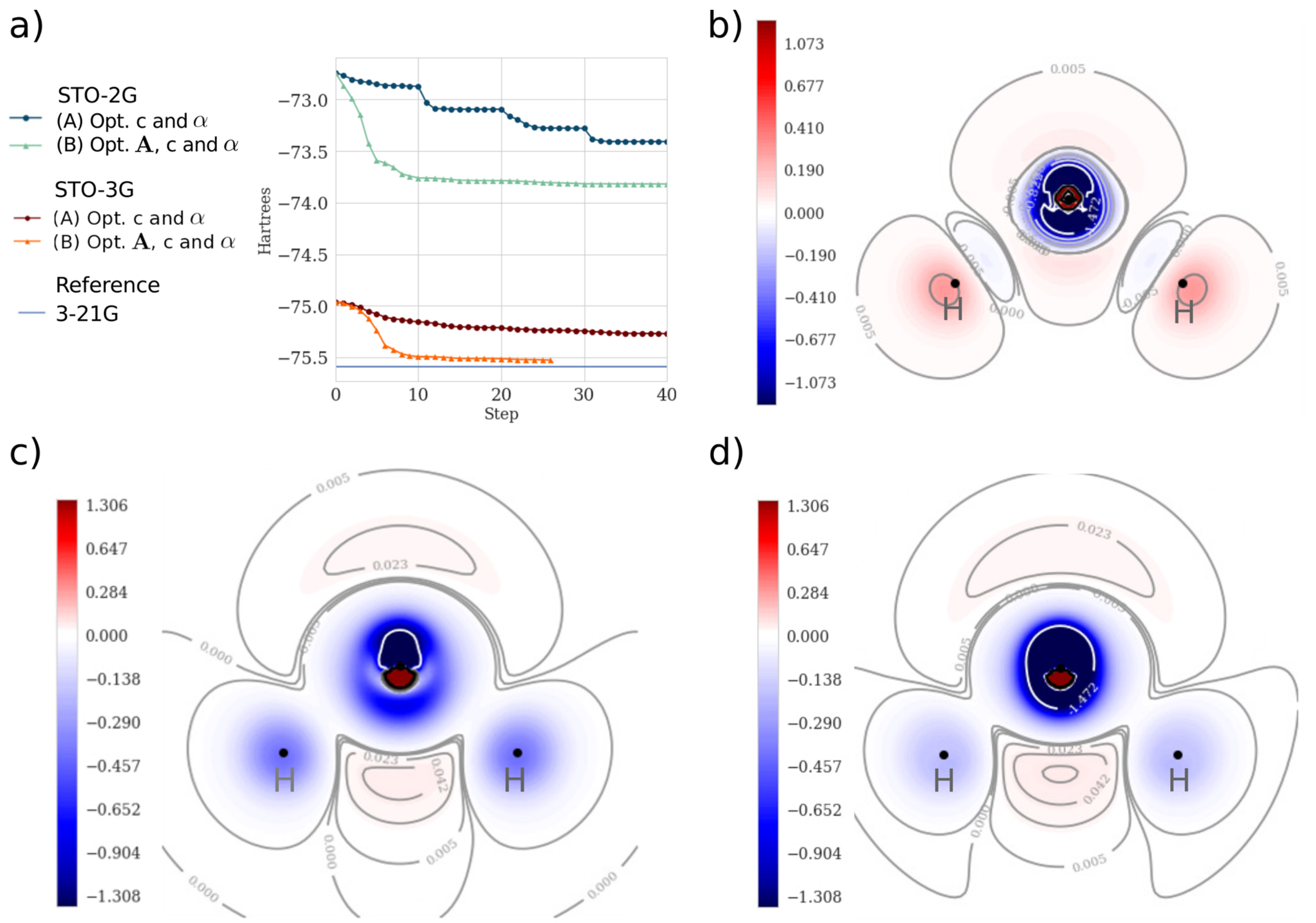

Figure 3. One-electron basis function optimizations of H_2O. (a) Optimization steps of STO-3G and STO-2G with different optimization schemes. (A) Optimizing exponents and coefficients 10 steps each twice, and (B) optimizing exponents and coefficients together, followed by optimizing positions. (b) Contour of the difference in electronic density between the STO-3G basis and the optimized one-electron basis functions under scheme (B). (c) Contours of the difference in electronic density between the conventional STO-3G basis set and the reference 3-21G basis set. (d) Contour of the difference in electronic density between the optimized (scheme (B)) STO-3G basis set and the reference 3-21G basis set. An increase of density on the optimization is displayed in blue and a decrease is in red.

based quantum chemistry methods, one and two electron integrals are typically defined by an element-wise array assignment (e.g., $A[i,j] = k$). This nonvectorized assignment represents a major challenge for backward mode regarding the amount of memory needed to store the computational graph as well as intermediate variables and derivatives.

The most critical component for our HF implementation in *DiffiQult* is matrix diagonalization. In some AD libraries such as *autograd*,[65] this matrix operation is considered as an elementary operation, which can be implicitly differentiated to obtain its adjoints and derivatives, respectively for each mode. In backward mode, the analytical expression for the adjoint of the eigenvectors is in principle available. However, the adjoints of the eigenvectors corresponding to repeated eigenvalues are not differentiable;[3,64] see Supporting Information. Therefore, we cannot use backward differentiation for matrix diagonalization of systems with degenerate molecular orbitals. Since we aim to compute general molecular systems, we exclude the backward mode for our implementation of *DiffiQult*. This leaves the forward mode as a possible option to circumvent the challenges of repeated eigenvalues. For the forward mode, the analytical expressions of the derivatives of eigenvectors are known, even for the degenerate case.[66] This method relies on computing the *n*th-order derivative of the eigenvalues such that its diagonals are distinct and on computing the n + 1th-order derivative of the original matrix that needs to be diagonalized; see Supporting Information. Therefore, we would need an implementation that would depend on a case-by-case analysis. Alternatively, Walter et al.[67] proposed a general algorithm to compute the diagonalization, based on univariate Taylor polynomials (Supporting Information),[1,63] implemented in Algopy.[63] This approach is mathematically equivalent to forward differentiation and considers the repeated eigenvalue problem. For further details, we refer the reader to the Supporting Information.

Even though we may consider reverse mode as a more efficient way for our implementation given the large number of input parameters and the small number of output variables, after this analysis, we conclude that an HF implementation is required to be based on the forward mode. Regarding the AD library, we have chosen Algopy,[63] since it supports both AD modes, provides matrix diagonalization for repeated eigenvalues, and requires only minimal modifications to calculate gradients of functions implemented in plain Python.

Finally, once we have implemented an autodifferentiable HF algorithm in Algopy, we use a gradient-based optimization to optimize Gaussian centers, widths, and contraction coefficients either together or separately. We use the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm[68] implemented in the *scipy* module. As recommended in ref 56, we take the natural logarithm to optimize the Gaussian exponents. No unexpected or unusually high safety hazards were encountered during the course of this study.

5. RESULTS

We tested our implementation by optimizing the STO-2G as well as the STO-3G minimal basis sets for the small molecules H_2O, HF, NH_3, CH_4, and CH_2O. Since we can obtain the gradients with respect to any input parameter, *DiffiQult* has the freedom to select different optimization procedures. Here, we illustrate two schemes: (A) optimizing the Gaussian exponents and contraction coefficients, sequentially, and (B) optimizing the contraction coefficients and exponents, followed by an optimization of the Gaussian centers. For the example of H_2O, the improvement of the energies for each optimization step is illustrated in Figure 3. We find that the most efficient way to optimize the HF energy is by employing scheme (B) since it already converges after 10 basis set optimization steps. For a general assessment of which method works better than the other, we need to consider the trade-off between reaching fast convergence and computation time. For example, scheme (B) requires more time to perform a single optimization step since it requires computing more gradients for a larger number of parameters due to the line-search procedure within the BFGS algorithm. All optimizations were done until finding an infinite norm of the gradient of 10^{-5} or a total of 10 steps, respectively. Table 1 displays HF energies for optimized and nonoptimized

Table 1. Hartree–Fock Energies in Hartrees Test Molecules of the Nonoptimized and Optimized (Scheme (B)) basis sets STO-2G and STO-3G[a]

	basis				
	STO-2G		STO-3G		
molecule	none	Opt. *coef*, α and **A**	none	Opt. *coef*, α and **A**	reference: 3-21G
HF	−95.60	−97.03	−98.57	−99.38	−99.46
H_2O	−72.74	−73.82	−74.96	−75.52	−75.59
NH_3	−53.82	−54.65	−55.45	−55.83	−55.87
CH_4	−38.59	−39.32	−39.72	−39.96	−39.98
CH_3F	−133.09	−134.96	−137.17	−137.43	−138.28
CH_2O	−109.02	−110.54	−112.35	−112.72	−113.22

[a]As a reference, we show results for the larger 3-21G basis set.

basis sets for selected small molecules. The optimization scheme (B) results in an improvement of up to 0.18 hartree per electron.

The minimal basis sets we optimized lacked in flexibility to correctly represent polarization and dispersion in the core molecular orbitals. For instance, hydrogen contains only a single atom centered s-type orbital that is insufficient to display changes in the density induced by the surrounding charges. By optimizing the parameters of the atomic orbital of each hydrogen, we can partially take into account polarization effects. As is depicted in Figure 3b, the optimization of the basis STO-3G of H_2O shifts the electronic density from the regions around the hydrogen atoms toward the bond regions. In the case of the oxygen, as it is shown in Figure 3c,d, the number of basis function is not sufficient to represent both the bond and the density around the oxygen itself, even after the optimization. Therefore, corrections to the core atomic orbitals of oxygen would need to include a greater number and higher angular momentum one-electron functions.

Finally, we discuss a common convergence problem of the HF method that can affect our fully variational HF implementation. It appears in our examples mainly in the line-search, when the optimizer by chance tests the parameter for which the SCF is difficult to get converged. In principle, this problem can be circumvented by suitable convergence strategies in the HF algorithm.

6. CONCLUSION AND PERSPECTIVE

AD offers a promising alternative solution for computing accurate derivatives of electronic structure methods. In this manuscript, we implemented *DiffiQult*, which serves as a proof-of-concept that helps us to develop an understanding of the capabilities of AD in quantum chemistry. Specifically, we presented and discussed the use of AD in the context of a fully variational HF method, which contains most of the mathematical components of other electronic structure methods. By using the *Algopy* AD library, we calculated gradients of any parameter with just minimal adjustments in the source code of the canonical HF energy, without any explicit implementation of a single derivative. With these gradients at hand, we are able to fully minimize the energy with respect to any parameter of the Gaussian one-particle basis. As a result, we capture, to some extent, polarization effects with a reduced number of atomic orbitals. Since the essential functions of many quantum chemistry methods are similar to the ones present in HF, we plan to extend *DiffiQult* to post-HF methods in future work.

DiffiQult can be seen as a general tool to obtain molecular tailored basis functions, that can be used as a starting point for other variational methods, e.g., FCI. An emerging application could be in the field of quantum computing for quantum chemistry,[69] where the size of one-electron basis function is constrained by the number of qubits available in state-of-the-art hardware.[70−74] Thus, experimental demonstrations of quantum algorithms for chemistry have been limited to conventional minimal basis sets.[74,75] Here, the fully variational setting of *DiffiQult* could offer the advantage to optimize initial parameters of atomic orbitals, which could increase the accuracy of variational quantum chemistry simulations,[69] while keeping the number of basis functions small.

Finally, the analysis of the advantages of AD technologies in the implementation of *DiffiQult* demonstrates that AD has a huge potential in future implementations. The AD tools could extend quantum chemistry methods in many ways. For example, in general, it is possible to mix different differentiation modes and approaches. We could use the forward mode to compute gradients of element-wise matrix definitions (or in general for complex computational graphs) and use the backward mode for vectorized functions. Furthermore, AD could be combined with symbolic algebra and automated code generation[76−78] to build a general tool-chain to create software packages capable of computing a function and computing gradients with an AD library.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.7b00586.

Derivatives and adjoints of eigenvectors (S1). Description of a method used to compute the derivatives of repeated eigenvalues in forward mode, Univariate Taylor Arithmetic (S2) (PDF)

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