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Auxiliary Basis Sets for Grid-Free Density Functional Theory

Kurt Raymond Glaesemann
Iowa State University

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

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Abstract

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Keywords

Basis sets, Density functional theory

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Comments

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Auxiliary basis sets for grid-free density functional theory

Kurt R. Glaesemann and Mark S. Gordon

Chemistry Department, Iowa State University, Ames Laboratory, United States Department of Energy, Ames, Iowa 50011

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Density functional theory (DFT) has gained popularity because it can frequently give accurate energies and geometries. The evaluation of DFT integrals in a fully analytical manner is generally impossible; thus, most implementations use numerical quadrature over grid points. The grid-free approaches were developed as a viable alternative based upon the resolution of the identity (RI). Of particular concern is the convergence of the RI with respect to basis set in the grid-free approach. Conventional atomic basis sets are inadequate for fitting the RI, particularly for gradient corrected functionals [J. Chem. Phys. **108**, 9959 (1998)]. The focus of this work is on implementation of and selection of auxiliary basis sets. Auxiliary basis sets of varying sizes are studied and those with sufficient flexibility are found to adequately represent the RI. © 2000 American Institute of Physics. [S0021-9606(00)30424-X]

I. INTRODUCTION

In recent years, density functional theory (DFT), formulated in terms of the spin densities (n_α, n_β), has gained popularity as a method for determining molecular properties and structures as an alternative to *ab initio* wave functions. Functionals of the density have been fit to the uniform electron gas,^{1,2} and have incorporated corrections that depend upon the density gradient.³⁻⁵ “Hybrid functionals” that mix in Hartree–Fock exchange are reported to help correct for the inadequacies of a single-reference wave function.^{6,7} DFT can frequently give energies, relative energies, and geometries more accurately than second-order perturbation theory, with significantly less computational expense,⁸ although reports of failures of DFT are not uncommon in the literature.⁹⁻¹¹

Evaluating integrals over functions of the density in a closed analytic form is usually impossible, because the functional forms involve very complicated functions of the density. Most DFT implementations evaluate the integrals using numerical quadrature over a finite set of grid points often organized in atom centered Lebedev spheres:¹²⁻¹⁴

$$\int f(n_\alpha, n_\beta, \nabla n_\alpha, \nabla n_\beta) d\vec{r} \approx \sum_i f(n_\alpha(i), n_\beta(i), \nabla n_\alpha(i), \nabla n_\beta(i)) \overline{\Delta r(i)}. \quad (1)$$

Dunlap discussed how integrating over a finite grid can lead to numerical instabilities.¹⁵ An $X-\alpha$ specific grid-free approach was developed to avoid these difficulties.¹⁵⁻¹⁷ Recently, a more general grid-free approach was proposed by Almlöf and Zheng (AZ)^{18,19} and has been further developed by us and others.²⁰⁻²² These grid-free approaches involve approximations that introduce errors that can be systematically eliminated by increasing the basis set size, and are independent of the coordinate system chosen.

The primary focus of the current work is on the basis set convergence properties of auxiliary basis sets within AZ grid-free DFT for the first row of the periodic table. The auxiliary basis sets are used to converge the resolution of the identity (RI).²³ Several prototypical systems are studied to explore the convergence of properties as a function of the basis set. These results demonstrate in detail the basis set dependence of the grid-free approach. In the previous work convergence of the RI was approached by enlarging the atomic basis set. This was successful, but it made separating basis set convergence from RI convergence difficult and resulted in extensive use of computational resources, because expensive two-electron integrals grow with the basis set. Bernholdt and Harrison have recently considered auxiliary basis sets for fitting RI–MP2, an approach to second-order perturbation theory using the resolution of the identity.²⁴

II. A GRID-FREE APPROACH TO DFT

The several approximations used within the grid-free approach²⁰ implemented in GAMESS²⁵ are briefly reviewed here. The accuracy of these approximations is directly related to the completeness of the basis. The initial simplification is to split portions that depend on functions of the density, such as n_α , n_β , ∇n_α , and ∇n_β , using the following expression:

$$\int \chi_i f \cdot g \chi_j d\vec{r} \approx \sum_m \int \chi_i f \theta_m d\vec{r} \cdot \int \theta_m g \chi_j d\vec{r}. \quad (2)$$

Equation (2) is exact if $\{\theta_m\}$ is a complete orthonormal set; otherwise, one expects some dependence of the calculation on the size of the basis set. Calculating the spin-polarization $\zeta = (n_\alpha - n_\beta)/(n_\alpha + n_\beta)$ requires using the RI in Eq. (2) to combine $f = (n_\alpha + n_\beta)^{-1}$ and $g = (n_\alpha - n_\beta)$ to form ζ .

A second “spectral” RI must be used to evaluate the complicated integrals involving functions of the density and the density gradient.²⁶ This method [see Eq. (3) below], without loss of generality,²³ assumes that the matrix of inte-

grals over the density has been transformed to an orthonormal basis set in which this matrix is diagonal. The function of the integral is assumed to be the integral of the function:

$$\int \theta_i f(n) \theta_j d\vec{r} \approx f \left(\int \theta_i n \theta_j d\vec{r} \right) \approx f(\lambda_i) \delta_{ij}, \quad (3)$$

where λ_i is an eigenvalue of the matrix $M[n]_{ij} = \int \theta_i n \theta_j d\vec{r}$. Equation (3) is exact in a complete basis. In DFT, n is the density, although Eq. (3) does not assume this. Therefore, once the integrals over n are determined, the integrals over any well-behaved function of n , such as $n^{-1/3}$, can be readily obtained.

The matrix representation of the density $M[n]$ is calculated from the first-order density matrix D and atomic orbitals i, j, k , and l without using the RI:

$$M[n]_{ij} = \int \chi_i n \chi_j d\vec{r} = \sum_{kl} D_{kl} \int \chi_i \chi_k \chi_l \chi_j d\vec{r}. \quad (4)$$

The density gradient is evaluated dimensionlessly as follows:

$$\int \chi_\mu \left(\frac{\nabla n}{n^{4/3}} \right) \chi_\nu d\vec{r} = 3 \left[\int \chi_\mu n^{1/3} \nabla \chi_\nu d\vec{r} - \int \chi_\mu \nabla (n^{1/3} \chi_\nu) d\vec{r} \right] \quad (5a)$$

$$\approx 3 \sum_m \left[\int \chi_\mu n^{1/3} \theta_m d\vec{r} \cdot \int \theta_m \nabla \chi_\nu d\vec{r} - \int \chi_\mu \nabla \theta_m d\vec{r} \cdot \int \theta_m n^{1/3} \chi_\nu d\vec{r} \right]. \quad (5b)$$

Due to the presence of derivative terms, basis functions of one higher angular momentum are needed in order for this application of the RI to be accurate.

The AZ grid-free DFT approach is also applied to the computation of nuclear gradients.^{19,20} The RI is only applied once in Eq. (6):

$$\int \left(\frac{\partial \chi_r}{\partial x} \right) \hat{K}^{\text{DFT}} \chi_s d\vec{r} \approx \sum_m \int \left(\frac{\partial \chi_r}{\partial x} \right) \theta_m d\vec{r} \cdot \int \theta_m \hat{K}^{\text{DFT}} \chi_s d\vec{r}, \quad (6)$$

where x is a nuclear coordinate and \hat{K}^{DFT} is the DFT exchange-correlation operator. As in Eq. (5), higher angular momentum functions are necessary to properly treat the derivative terms. If the $\{\theta\}$ is too small, inconsistencies between the energy and the gradients can cause problems optimizing. Similar problems have been found within grid-based methods, if the grid is too coarse.¹⁵⁻¹⁷

III. AUXILIARY BASIS SETS FOR FITTING THE RESOLUTION OF THE IDENTITY

Since a large basis set is necessary for the RI to be accurate, during the DFT portion of the calculation, an auxiliary basis set is required. Before the SCF procedure is begun, the auxiliary basis set is built. Each atom is given a set of even-tempered basis functions²⁵ that include angular momentum functions from zero to one higher than that of the

valence space. The valence space is defined as s for H–He, sp for Li–Ar, and spd for K–Xe. In this work, we focus on H–F.

The two index one-electron dipole velocity and overlap integrals are calculated over both the AO basis and the auxiliary basis and stored to disk. Using the overlap matrix S , the matrix W is generated (analogous to the linear combination of atomic orbitals matrix C). W transforms both AO and the auxiliary orbitals to an orthonormal set, because $W^\dagger S W = I$ (analogous to $C^\dagger S C = I$). During the generation of W , the MO's are not allowed to contain any auxiliary character. This is accomplished by making the auxiliary space orthogonal to the entire MO space. Due to the size of the auxiliary basis set, it is crucial to test for linear dependencies. Linearly dependent functions are removed from the space by zeroing out a column of the W matrix.

The matrix representation of the density $M[n]$ is generated every SCF cycle according to Eq. (4). The k and l indices run only over the AO basis because the auxiliary basis functions contain no electron density, but indices i and j run over the entire basis. This requires the calculation of $N^2 M^2$ integrals, where N is the number of AO's and M is the number of AO's plus the number of auxiliary functions. At the end of each SCF cycle, only the parts of the resulting matrices that correspond to the MO space are saved. For gradient calculations, the entire exchange-correlation potential is saved for use later in Eq. (6).

The grid-free approach outlined above has been used to implement several DFT functionals in GAMESS. Several functionals are used to examine different applications of the RI and are listed below. Energy gradients are calculated to demonstrate the RI in Eq. (6), which is independent of the functional.

(1) $X-\alpha^1$ has neither $n_\alpha n_\beta$ cross terms nor gradient dependence. It only involves the use of the RI in Eq. (3). For the uniform electron gas value of $\alpha=2/3$, this is called the Slater functional.

(2) $\text{VWN5}^{2,8,27,28}$ has no gradient dependence. It uses the RI in Eq. (2) to multiply together terms that depend on $\zeta = (n_\alpha - n_\beta)/(n_\alpha + n_\beta)$ and terms depending on n . Functions of ζ and n are generated using the RI in Eq. (3).

(3) The Becke88²⁹ gradient corrected exchange functional relies on the RI in Eq. (5) to generate $y^2 = (\nabla n)^2/n^{8/3}$, the dimensionless density gradient. The RI in Eq. (3) is used to generate functions of both n and y^2 . Finally, the RI in Eq. (2) is used to combine all the terms. The DePristo–Kress functional³⁰ is a predecessor to Becke88 that is similar in design and use of the RI. It is included to demonstrate that the Becke88 grid-free results are not coincidental, although no comparison to a grid based result is available for this functional.

All comparisons presented below are made to the grid based DFT code in Gaussian 94.³¹ The grid used in all calculations is a pruned grid of (75, 302), in which there are 75 radial shells and 302 angular points per shell. This results in about 7000 points per atom. This is the default integration grid in Gaussian 94. Both GAMESS and Gaussian 94 calculate all nonexchange-correlation terms explicitly from Ψ , rather than from n .

TABLE I. Hydrogen atom with the Slater functional.

Auxiliary basis set	Energy (hartree)	Difference from grid (kcal/mol)	Percent difference from grid
Grid	-0.455670	0.00	0.00
None	-0.462003	-3.97	-1.39
5s	-0.455904	-0.15	-0.05
9s	-0.455684	-0.01	-0.00
9s+	-0.455684	-0.01	-0.00

The auxiliary basis sets are based on the correlation-consistent basis sets of Dunning *et al.*³² It has been shown that by using large auxiliary basis sets, RI-MP2 can be made exact, but much smaller basis sets suffice to get accurate energy differences.^{24,33} The initial choice of auxiliary functions was a set of even-tempered³⁴ functions that spanned the same exponent range as the aug-cc-pVDZ basis. This is different than the initial RI-MP2 uncontracted correlation consistent basis sets used by Bernholdt and Harrison. The basis sets in this work are augmented in an even-tempered manner. The auxiliary basis set notation is as follows: “5s3p” means that there are five *s* gaussians and three sets of *p* gaussians that span the same exponent range as the *s* and *p* shells of the aug-cc-pVDZ basis set of Dunning. “5s+3p+-” means that there are two additional diffuse *s* gaussians, one additional set of tight *p* gaussians, and one additional set of diffuse *p* gaussians. When multiple atoms are present, the heavy atom will be listed first and the hydrogen atom last, as in 10s5p2d/5s2p. This notation is used throughout the remainder of this work. In our previous work, the even-tempered basis set approach was very slow to converge the RI, because the basis was not augmented with diffuse or tight functions. Therefore, 10 *s* functions and 20 *s* functions spanned nearly the same range of exponents and gave similar results. Results for calculations that only used the atomic basis set for resolving the identity are appropriately labeled “no auxiliary basis set.”

IV. GRID-FREE DFT RESULTS

A. Hydrogen atom

Hydrogen was first studied with the Slater functional. The cc-pVDZ basis set is used as the atomic basis set for both the grid and the grid-free calculations (Table I). Note that the “exchange” energy for single electron systems is present to cancel out the self-repulsion terms. The addition of 5s (to match aug-cc-pVDZ) gaussians is found to reduce the difference in total energy relative to the grid based approach by over an order of magnitude to 0.15 kcal/mol, but the error is still larger than desirable. Next, we add four more *s* functions, such that each exponent is between two of those in the original 5s set. This yields a 9s auxiliary basis set whose energy differs from the grid-based approach by less than 0.01 kcal/mol (Table I). Because most calculations involve H within molecules, an additional diffuse *s* function is added to help account for longer-range interactions, although 9s and 9s+ give the same results for the H atom. Therefore, the RI used in Eq. (3) is found to converge very quickly, as

TABLE II. Hydrogen atom with the *B*-null functional.

Auxiliary basis set	Energy (hartree)	Difference from grid (kcal/mol)	Percent difference from grid
Grid	-0.496403	0.00	0.00
None	-0.479810	10.49	3.37
9s+3p	-0.493721	1.68	0.54
9s+3p+	-0.494663	1.09	0.35
9s+3p-	-0.495862	0.34	0.11
9s+3p+-	-0.495869	0.33	0.10

was found in our previous work. All subsequent calculations focus on more complicated applications of the RI. Auxiliary basis sets are included in the supplementary material.

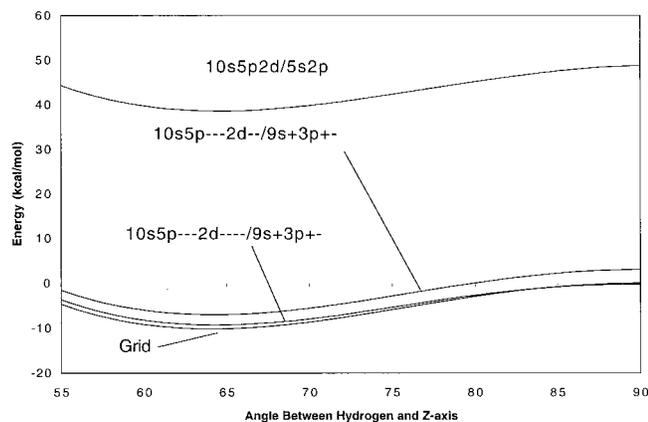
Gradient-corrected calculations on H with the *B*-null functional (Becke88 exchange and no correlation) are summarized in Table II. This functional requires that the auxiliary basis set contain *p* functions due to the use of the RI in Eq. (5). The initial auxiliary basis set is the one optimized for the Slater functional (9s+) plus three additional sets of *p* functions to yield the 9s+3p auxiliary basis set. The energy obtained using this basis set differs from that of the grid-based approach by over 1 kcal/mol, but the difference is much smaller than that of the grid-free approach with no auxiliary basis set. A set of diffuse *p* functions reduces the difference further, and adding a set of tight *p* functions (without the diffuse set of *p* functions) reduces the difference to 0.34 kcal/mol (0.11%). Therefore, these are combined to form the 9s+3p+- auxiliary basis set.

B. Nitrogen atom

Atomic N was studied with an unrestricted wave function, the *B*-null functional and the cc-pVDZ basis set³² as the atomic basis set (Table III). The initial auxiliary basis is 10s5p2d, because it involves the same number of gaussians as aug-cc-pVDZ. This auxiliary basis set corrects the poor behavior that occurs if no auxiliary basis set is used. The energy difference relative to the grid-based method is still rather large, 38.57 kcal/mol. Because the aug-cc-pVDZ basis does not include *p* functions for the inner shell, two tight sets of *p* functions were added. The energy difference relative to

TABLE III. Nitrogen atom with the *B*-null functional.

Auxiliary basis set	Energy (hartree)	Difference from grid (kcal/mol)	Percent difference from grid
Grid	-54.381 41	0.00	0.000
None	-54.830 14	281.58	-0.825
10s5p2d	-54.319 94	38.57	0.113
10s5p--2d	-54.368 40	8.16	0.024
10s5p---2d	-54.369 01	7.78	0.023
10s5p----2d-	54.366 18	9.56	0.028
10s5p----2d--	-54.375 76	3.54	0.010
10s5p----2d---	-54.375 55	3.67	0.010
10s5p----2d----	-54.375 43	3.75	0.011
10s5p+----2d+---	-54.375 95	3.43	0.009
10s5p+----2d+----	-54.376 33	3.18	0.009

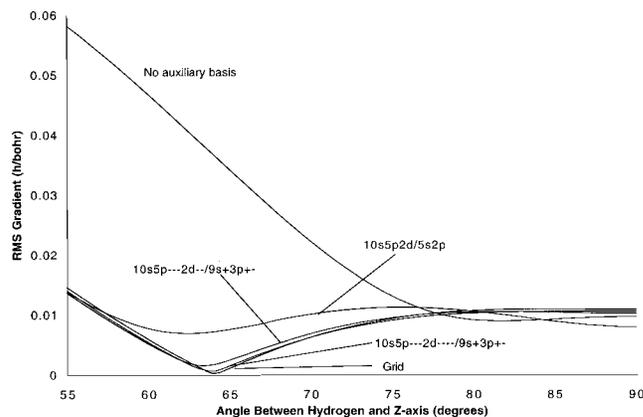
FIG. 1. NH_3 bend potential with B -null and cc-pVDZ basis set.

the grid method is reduced by 30 kcal/mol to 8.2 kcal/mol. The p functions improve the accuracy of the RI in Eq. (5) for atomic s functions and the RI in Eqs. (2) and (3) for atomic p functions. A third set of tight p functions only results in a slight improvement of 0.4 kcal/mol, so no additional sets of p functions were added. Tight d functions were added next, because polarization functions present in atomic basis sets have exponents designed for the bonding region and not near the atomic center. Adding two sets of tight d functions reduces the difference relative to the grid to 3.54 kcal/mol. Addition of a third and fourth set of tight d functions produces energy differences of 3.67 kcal/mol and 3.75 kcal/mol, respectively. Addition of a set of diffuse p and d functions results in a small improvement. Attempts to improve the agreement between the grid and grid-free results with the addition of f functions provided little change in the grid-free energy (0.1 kcal/mol with three f functions); the same is true for the addition of two tight s functions (0.02 kcal/mol).

C. NH_3 bend potential

For loose grids, Werpinski and Cook¹⁶ found that the NH_3 bend potential obtained with grid based DFT could become asymmetric. For small basis sets, the AZ grid-free approach gives symmetrical, but inaccurate curves.²⁰ As the basis set is increased, the grid-free bend potential approaches the correct behavior. The atomic basis set used in the present calculations is cc-pVDZ.³² The NH bond distance is fixed at 1.0496 Å, to allow easy comparison to previous work.^{16,20} Because the NH bond distance is optimized for the $X-\alpha$ functional, the gradient will never go exactly to zero for other functionals. The functional used here is B -null.

Potential energy surfaces as a function of angle are presented in Fig. 1. With no auxiliary basis set, the curve is 0.5 Hartree too low, and the shape does not match the shape of the grid-based curve (this curve is not presented in Fig. 1). Adding the initial $10s5p2d/5s2p$ basis set (even-tempered uncontracted aug-cc-pVDZ) yields a properly shaped curve; the energy differs from that of the grid curve by an average of 38 kcal/mol. Enlarging the auxiliary basis set to $10s5p---2d---/9s+3p+-$, reduces the average difference across the entire PES to 3 kcal/mol. As was found in the RI-MP2 analysis,²⁴ accurate relative energies are obtained

FIG. 2. NH_3 bend potential with B -null and cc-pVDZ basis set.

with smaller basis sets than required for absolute energies. Using the auxiliary basis set $10s5p---2d---/9s+3p+-$ optimized for H and N, the maximum difference on the PES between the grid-free and the grid-based methods is reduced to 1.0 kcal/mol. The range of differences for this basis set is 0.25 to 1.01 kcal/mol.

The Cartesian RMS gradient of NH_3 , shown in Fig. 2, provides insight into the RI used in Eq. (6). Without an auxiliary basis set, the curve is completely wrong. The RI is so poorly converged that the gradient is little more than random numbers. Using the $10s5p2d/5s2p$ auxiliary basis set moves the minimum to within 2° of the grid minimum, but the grid-free RMS gradient decreases less than that of the grid. The $10s5p---2d---/9s+3p+-$ basis set gives a curve that is very similar to the grid based curve, except for the lowest portions of the curve, where the RMS values are larger than the grid based values. The $10s5p---2d---/9s+3p+-$ basis set, optimized for the N and H atoms, gives the same minimum RMS gradient as the grid method. The curves are almost indistinguishable. Therefore, convergence of the nuclear gradient RI in Eq. (6) requires tight auxiliary basis functions. Several sets of d functions are needed for the RI to be accurately represented. This can be explained by the bonding in NH_3 . The atomic p orbitals on N are important in bonding and therefore d functions (one higher angular momentum) are needed in order for the nuclear gradient resulting from these bonds to be accurate.

D. Nitrogen molecule

N_2 was shown in our previous work to require a large and cumbersome atomic basis set to get accurate results because an auxiliary basis set was not used. In the current work (Table IV), the cc-pVTZ basis set and unrestricted wave functions are used for N. The B -null functional is used in order to allow easy comparison to our previous work. Experimental results are also presented.^{35,36} With no auxiliary basis set, the bond length differs from the grid method by 0.26 Å and the binding energy differs by 39 kcal/mol. Obviously, an auxiliary basis set is needed to get accurate geometries and relative energies. Although the $10s5p2d$ auxiliary basis set predicts the bond length to within 0.010 Å of the grid method, the binding energies differ by 9.1 kcal/mol. The

TABLE IV. N₂ with the *B*-null functional and aug-cc-pVTZ.

Auxiliary basis set	Binding energy (kcal/mol)	Bond length (Å)
Experiment	228.3	1.098
Grid	178.5	1.113
None	139.7	1.376
10s5p2d	187.6	1.123
10s5p---2d--	181.8	1.115
10s5p---2d----	183.4	1.113
10s5p+---2d+-	179.3	1.115
10s5p+---2d+----	178.4	1.114

10s5p---2d-- basis set predicts the bond length to within 0.002 Å of the grid method and binding energies to within 3.4 kcal/mol of the grid method. The 10s5p---2d---- auxiliary basis set gives the same geometry as the grid but the binding differs by 4.9 kcal/mol. Addition of the diffuse *p* and *d* functions to form 10s5p+---2d+- and 10s5p+---2d+---- improve agreement with the grid method to 0.8 kcal/mol and 0.1 kcal/mol, respectively. Therefore the RI's appear to be converged for the 10s5p+---2d+---- auxiliary basis set.

E. Other first-row compounds

The auxiliary basis sets developed for nitrogen have been generalized to elements Li through Ne. The aug-cc-pVDZ basis sets were used to provide the exponents for the tightest and most diffuse gaussian functions of the initial

TABLE VI. H₂O with *B*-null functional and 6-31G**.

Auxiliary basis set	O-H bond Å	H-O-H angle
Grid	0.987	102.1°
None	0.964	120.6°
10s5p2d/5s2p	1.000	97.9°
10s5p---2d--/9s+3p+-	0.991	100.9°
10s5p---2d----/9s+3p+-	0.990	100.7°
10s5p+---2d+-/9s+3p+-	0.991	100.8°
10s5p+---2d+----/9s+3p+-	0.991	101.0°

10s5p2d/5s2p auxiliary basis set. Results for both the 10s5p2d/5s2p auxiliary basis set and the larger auxiliary basis sets are presented below.

CH₂. Experimental structures and relative energies^{37,38} for the ¹A₁ and ³B₁ states of CH₂ are compared in Table V for the *B*-null, DePristo-Kress, and *B*-VWN5 functionals. The AO basis set used here is cc-pVTZ.³² The ³B₁ state was optimized with a restricted open shell wave function. Using no auxiliary basis set results in H-C-H bond angles that differ from the grid based approach by over 50° for all three functionals. The C-H bond distances differ from the grid based predictions by 0.3 Å. The predicted ¹A₁-³B₁ splittings differ from the grid based values by as much as 0.33 eV. As expected, the RI is not adequately represented by the CH₂ atomic basis set. The 10s5p2d/5s2p auxiliary basis set reduces the difference between the grid-free and grid angles, with the largest difference being 9.2° for the *B*-VSN5 triplet. The largest bond length difference is reduced to 0.014 Å.

TABLE V. CH₂ with pVTZ.

Auxiliary basis set	¹ A ₁ CH bond (Å)	¹ A ₁ H-C-H angle	³ B ₁ CH bond (Å)	³ B ₁ H-C-H angle	¹ A ₁ - ³ B ₁ splitting (eV)
Experiment	1.11	102°	1.07	134°	0.369-0.390
Becke88 functional					
Grid	1.135	100.6°	1.096	131.8°	0.87
None	1.420	61.1°	1.259	83.5°	0.55
10s5p2d/5s2p	1.151	96.7°	1.100	131.7°	0.97
10s5p---2d--/9s+3p+-	1.139	100.2°	1.098	132.0°	0.93
10s5p---2d----/9s+3p+-	1.137	100.7°	1.098	132.1°	0.92
10s5p+---2d+-/9s+3p+-	1.138	100.2	1.098	131.9	0.92
10s5p+---2d+----/9s+3p+-	1.138	100.5	1.098	131.5	0.92
DePristo functional					
None	1.416	62.0°	1.283	81.2°	0.29
10s5p2d/5s2p	1.144	99.1°	1.099	132.0°	0.91
10s5p---2d--/9s+3p+-	1.136	100.6°	1.094	132.5°	0.89
10s5p---2d----/9s+3p+-	1.133	101.4°	1.094	132.1°	0.89
10s5p+---2d+-/9s+3p+-	1.135	100.6°	1.094	132.6°	0.89
10s5p+---2d+----/9s+3p+-	1.135	100.7°	1.094	131.0°	0.89
<i>B</i> -VWN5 functional					
Grid	1.115	101.0°	1.079	134.0°	0.38
None	1.411	60.5°	1.255	82.0°	0.12
10s5p2d/5s2p	1.129	97.5°	1.093	124.8°	0.36
10s5p---2d--/9s+3p+-	1.118	100.7°	1.077	133.7°	0.32
10s5p---2d----/9s+3p+-	1.116	101.3°	1.077	132.9°	0.32
10s5p+---2d+-/9s+3p+-	1.118	100.7°	1.077	133.0°	0.30
10s5p+---2d+----/9s+3p+-	1.117	101.0°	1.075	134.8°	0.31

TABLE VII. Bond lengths in several systems with B -null functional in Å.

Auxiliary basis set	Grid	None	$10s5p2d$ $/5s2p$	$10s5p---2d---$ $/9s+3p+-$	$10s5p----2d-----$ $/9s+3p+-$	$10s5p+---2d+---$ $/9s+3p+-$	$10s5p+----2d+-----$ $/9s+3p+-$
O ₂ bond	1.249	1.320	1.292	1.254	1.249	1.255	1.252
F ₂ bond	1.460	1.589	1.517	1.455	1.446	1.463	1.457
Terminal H–B bond in B ₂ H ₆	1.207	1.198	1.210	1.208	1.208	1.208	1.208
Bridging H–B bond in B ₂ H ₆	1.344	1.592	1.361	1.348	1.347	1.348	1.347
B–B distance in B ₂ H ₆	1.815	2.603	1.870	1.829	1.824	1.829	1.825
Be–H bond in BeH ₂	1.350	1.349	1.355	1.350	1.350	1.350	1.350
Li–H bond in LiH	1.636	1.577	1.652	1.626	1.630	1.627	1.631

The error for the singlet–triplet splitting is reduced to no more than 0.09 eV. Enlarging the auxiliary basis set to $10s5p---2d---/9s+2p+-$ produces angles that are all within 0.4° of the grid values. The largest difference in predicted bond distances is reduced to 0.004 Å. The predicted singlet–triplet splittings all agree to within 0.06 eV of the grid-based method. The larger auxiliary basis set, $10s5p----2d-----/9s+2p+-$, provides no improvement with B-VWN5. The addition of diffuse p and d functions to the auxiliary basis set also provides little change. In all calculations, 3B_1 was correctly found to be the ground state. DePristo–Kress and B -null, both gradient corrected exchange functionals, have similar convergence properties with respect to the RI. For both the grid and grid-free approaches, the addition of electron correlation (e.g., via the VWN5 functional) is needed in order to avoid overestimating the $^1A_1-^3B_1$ splitting. For CH₂, auxiliary basis sets are found to be effective for functionals that depend on n_α , n_β , ζ , ∇n_α , and ∇n_β . Nuclear derivatives are also found to be reliable, since the grid and grid-free approaches predict similar geometries.

H₂O. The geometry of the ground state of water (Table VI) was optimized with the 6-31G** basis set³⁹ and the B -null functional. With no auxiliary basis functions, water is predicted have an H–O–H angle of 120.6°. The predicted H–O bond distances differ from the grid based value by 0.023 Å. Addition of the $10s5p2d/5s2p$ auxiliary basis set yields an HOH angle and OH bond length that are much closer to the grid values. The $10s5p---2d---/9s+2p+-$ auxiliary basis set reduces the differences in the predicted angle and bond length to 1.2° and 0.004 Å, respectively. The $10s5p----2d-----/9s+2p+-$ auxiliary basis set predicts a geometry that differs from the $10s5p-$

$---2d---/9s+2p+-$ auxiliary basis set by only 0.001 Å and 0.2°. Addition of diffuse p and d functions provides little change, so the geometry appears to be converged. Addition of diffuse and tight s functions also has little effect: less than 0.001 Å and 0.2°. Both methods differ slightly from the experimental⁴⁰ values of 0.958 Å and 104.45°.

Other molecules. The same auxiliary basis sets have been applied to several additional molecules with the B -null functional. High spin cases were all treated with unrestricted wave functions. The cc-pVTZ basis set was used as the atomic basis set. Interatomic distances are presented in Table VII. With no auxiliary basis sets, the largest variance from the grid-based result is 0.8 Å for the B–B distance in B₂H₆. The smallest difference from the grid-based approach is 0.009 Å for the terminal BH bond in B₂H₆. The $10s5p2d/5s2p$ auxiliary basis set improves the B–B distance to 1.870 Å, 0.055 Å different from the grid value. Indeed, the agreement of the interatomic distances predicted by the grid and grid-free approaches is improved for all but the B–H distance in Table VII upon adding the $10s5p2d/5s2p$ auxiliary basis set. Extending the auxiliary basis set to $10s5p---2d---/9s+2p+-$ reduces the largest difference between the grid and the grid-free distances to 0.014 Å. Other grid-free distances differ from the grid distances by less than 0.001 Å. The larger $10s5p----2d-----/9s+2p+-$ auxiliary basis set predicts all intra-atomic distances to within 0.014 Å of the grid distances. Addition of diffuse p and d functions results in only slight changes in bond distances.

Binding energies relative to the isolated atoms are predicted using the B -null functional and are presented in Table VIII. Since geometries are unreliable without an auxiliary basis set, the same is true for binding energies. The largest

TABLE VIII. Binding energies of several systems with B -null functional in eV.

Auxiliary basis set	Grid	None	$10s5p2d$ $/5s2p$	$10s5p---2d---$ $/9s+3p+-$	$10s5p----2d-----$ $/9s+3p+-$	$10s5p+---2d+---$ $/9s+3p+-$	$10s5p+----2d+-----$ $/9s+3p+-$
O ₂ binding	4.42	5.84	5.06	5.01	5.15	4.53	4.52
F ₂ binding	1.34	1.41	1.57	1.49	1.58	1.40	1.40
B ₂ H ₆ binding	20.66	15.63	21.75	20.82	20.90	20.70	20.68
BeH ₂ binding	5.26	7.61	5.41	5.28	5.28	5.28	5.28
LiH binding	1.57	2.52	2.30	1.57	1.58	1.57	1.58

TABLE IX. Timing comparisons between the grid-free and the grid-based approach for the Becke88 functional (CPU seconds).

Molecule	Grid	$10s5p---2d---/9s+3p+-$
N	53	8
N ₂	127	179
O	66	24
O ₂	138	267
B ₂ H ₆	6698	3370
BeH ₂	61	39
Propene	6782	14 173
LiH	61	21

difference relative to the grid-based prediction is 5.0 eV for B₂H₆. The $10s5p2d/5s2p$ auxiliary basis set reduces this to 1.1 eV. The $10s5p---2d---/9s+2p+-$ auxiliary basis reduces the difference to 0.16 eV or less, except for the difficult case of O₂. Significant improvement for O₂ requires the $10s5p+---2d+---/9s+2p+-$ auxiliary basis. This latter basis has essentially converged the RI for all molecules in the table. These diffuse functions are not needed for accurate geometries, but are needed for accurate energetics.

F. Timing comparisons

For several different auxiliary basis sets, timing comparisons for energy+gradient calculation are made to the grid-based method in Table IX. Because the $10s5p---2d---/9s+3p+-$ gives consistently reasonable results, it is used for comparison. In all cases, the CPU time required for the entire calculation is compared. The grid used is the default grid described above, which provides about 7000 points per atom. All calculations are run in direct mode. This means that these comparisons include the GAMESS and Gaussian integral routines, Fock matrix construction and solution of the SCF problem. Differences in convergence rates and the differences in work distribution between DFT and non-DFT portions of the codes also contribute to the timings differences. The main point is that the two approaches for evaluating DFT energies and gradients appear to require comparable times.

V. CONCLUSIONS

The grid-free approach to DFT provides an alternative to the grid-based approach. The resolution of the identity requires a more accurate basis set than does the wave function; therefore, an approach that utilizes auxiliary basis sets has been developed. In previous work, the RI was found to quickly converge for functionals that do not depend upon the gradient of the density. In this work, the gradient of the density RI in Eq. (5) is found to converge only after functions of angular momentum of one higher than the atomic basis set are included. Functions tighter than the normal atomic basis functions are also needed. Auxiliary basis sets that are adequate for giving proper energies are found adequate for giving proper gradients and therefore geometries. This is pleasant, since once one has an auxiliary basis set that gives reasonable energies, one does not have to extend it further still to give reasonable geometries.

For several of the systems studied here, there are residual differences between results predicted by the grid and the grid-free methods, even after the auxiliary basis set appears to have converged. This may be a consequence of a grid that is not fully converged. The two DFT methods appear to have similar CPU time requirements. We recommend the use of the $10s5p---2d---/9s+2p+-$ auxiliary basis set, for H-Ne (see EPAPS).⁴¹

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