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Accurate and balanced anisotropic Gaussian type orbital basis sets for atoms in strong magnetic fields

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In high magnetic field calculations, anisotropic Gaussian type orbital (AGTO) basis functions are capable of reconciling the competing demands of the spherically symmetric Coulombic interaction and cylindrical magnetic (B field) confinement. However, the best available *a priori* procedure for composing highly accurate AGTO sets for atoms in a strong B field [W. Zhu *et al.*, Phys. Rev. A **90**, 022504 (2014)] yields very large basis sets. Their size is problematical for use in any calculation with unfavorable computational cost scaling. Here we provide an alternative constructive procedure. It is based upon analysis of the underlying physics of atoms in B fields that allow identification of several principles for the construction of AGTO basis sets. Aided by numerical optimization and parameter fitting, followed by fine tuning of fitting parameters, we devise formulae for generating accurate AGTO basis sets in an arbitrary B field. For the hydrogen iso-electronic sequence, a set depends on B field strength, nuclear charge, and orbital quantum numbers. For multi-electron systems, the basis set formulae also include adjustment to account for orbital occupations. Tests of the new basis sets for atoms H through C ($1 \leq Z \leq 6$) and ions Li$^+$, Be$^+$, and B$^+$, in a wide B field range ($0 \leq B \leq 2000$ a.u.), show an accuracy better than a few μhartree for single-electron systems and a few hundredths to a few mHs for multi-electron atoms. The relative errors are similar for different atoms and ions in a large B field range, from a few to a couple of tens of millionths, thereby confirming rather uniform accuracy across the nuclear charge Z and B field strength values. Residual basis set errors are two to three orders of magnitude smaller than the electronic correlation energies in multi-electron atoms, a signal of the usefulness of the new AGTO basis sets in correlated wavefunction or density functional calculations for atomic and molecular systems in an external strong B field. *Published by AIP Publishing.* https://doi.org/10.1063/1.5004713

I. INTRODUCTION

Theoretical calculations for atoms and molecules subjected to a strong magnetic field (**B**) are indispensable to the interpretation of observed spectra and to ascertainment of the elemental composition of the atmosphere of those celestial bodies which exist in a strong B-field, e.g., the fields of magnetic white dwarfs (10^2–10^5 T) and neutron stars ($>10^7$ T). Although such large field strengths far exceed terrestrially available values, typical strong field effects nevertheless can be observed in laboratories in which static fields up to 30–40 T can be generated. Example systems include Rydberg atoms and the exciton in a semiconductor which possesses a small effective mass and a large dielectric constant.[1]

A non-perturbative approach is required to address the problem of atoms and molecules in a strong B field because the Coulomb force and the Lorentz force experienced by the electrons are on a par. A variety of methods thus has been devised to cope with the problem. They include formal mathematical analysis,[2] algebraic methods,[3] representation of the electronic wave function on a two-dimensional (2D) mesh,[4,5] or as a linear expansion in a suitably chosen basis. Basis sets used include finite-element schemes,[6] B-splines,[7] Slater-type orbitals (STO)[8] (which are more suitable for the weak B regime), Landau functions[9,10] (which are suitable for the very strong B field regime in which the adiabatic approximation is applicable[11]), or the product of both.[12] Recently Stopkowicz *et al.* extended coupled-cluster theory to the non-vanishing field regime, thus making standard quantum chemistry calculations available for atoms and molecules in strong B fields.[13] Those authors also found that standard basis sets were inadequate for B larger than about 1 a.u., which underscores the necessity of devising basis sets better than the currently available ones.

The medium to high field strength regime poses a formidable challenge to the calculations because of different symmetries of Coulomb and Lorentz interactions, neither of which is treatable as a perturbation. Current best practice for this difficult regime is to employ an anisotropic Gaussian type orbital (AGTO) basis. In such a basis, the exponential factor of the basis functions has different decay constants along the direction of the B field and the direction perpendicular to it. This anisotropy provides the flexibility required to describe the elongation of electron orbitals and densities along the field direction.

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AGTO basis sets were first introduced, to our knowledge, by Aldrich and Greene[14] and exploited extensively by Schmelcher and Cederbaum.[15] Successful applications are found in several studies of atoms in strong B fields.[16–20] As with ordinary GTO basis sets, the lack of a unique formal prescription for determination of the basis exponents compels the development of a physically sound prescription. Kappes and Schmelcher gave an optimization algorithm.[21] Because it must be used for every distinct combination of atomic configuration and field strength, computational cost and tedium are substantially larger than an ordinary ground-state GTO set. Furthermore, a good starting set of exponents is required.[16] Consequently, it is almost dauntingly hard and computationally costly to achieve near uniformity of quality of the generated basis sets. The magnitude of the residual basis set errors is uncontrolled, with no guarantee that those errors are insignificant nor close enough to uniform to support unbiased comparisons between different atomic configurations or different field strengths.

An alternative to case-by-case optimization is the use of nearly optimized basis sets. Kravchenko and Liberman (KL)[22] investigated one-electron systems, the hydrogen atom and the hydrogen molecular ion. They found that systematically constructed AGTO basis sets could provide absolute accuracy (relative to exact solution) of 10^{-6} hartree or better. We later improved the construction procedure and produced a set of formulae to generate nearly optimized basis sets based on a simple physical model. Details can be found in Ref. 23. Unfortunately, both the KL basis sets and ours rely upon multiple sequences of exponents (up through five) to reach relatively high accuracy, especially for large B. The inescapable result is a very large basis set size when compared to ordinary high-quality ground-state GTO sets. Such large sizes are quite unfavorable for use in highly correlated method calculations. Those methods typically have rather severe computational cost scaling with basis set cardinality (some power higher than four of basis set size times number of electrons). Therefore it is highly desirable to keep the basis set size as small as possible commensurate with desired accuracy. Experience with our multiple-sequence sets strongly suggests that we should have only one sequence of basis exponents or at most two if that is unavoidable.

For the $B = 0$ case, a huge variety of well-developed basis sets is available to choose from. Among them, two with very long lineages in quantum chemistry (beginning in the 1960s) are the Pople-type sets which use minimal representations of Slater-type functions or split-valence primitives to describe core and valence electron wavefunctions[24] and the Dunning correlation-consistent basis sets. The latter sets are composed of Gaussian primitives contrived to provide systematic convergence of the correlation energy from post-Hartree-Fock (HF) calculations.[25] For $B > 0$, there is no obvious single path to generalizing either the Pople or Dunning type set because of the infinite number of combinations of atomic nuclear charge Z and B field strength. Instead, one must seek appropriate formulations as a function of field strength and, as we will discuss below, orbital type as helpful parameters. In doing so, we follow the philosophy adopted by Dunning.[25] We explore (analytically and numerically) some simple paradigmatic systems to establish a few principles which should be applicable in general. We try to fathom, or at least rationalize, the underlying physical reasons that dictate those principles. We do some fine-tuning and test the resulting formulas for basis set generation with atoms H through C ($1 \le Z \le 6$, where Z = atomic number) over a very large range of B field strength ($0 \le B \le 2000$ a.u.). We take advantage of the availability of several highly accurate HF calculations[4,5,7,8] to assess the residual errors associated with the new basis set construction formulation.

Density functional theory (DFT) calculations are not included in this study because the extra errors originating from numerical grids and variety of exchange-correlation functionals would complicate comparison between our calculated results and reference values. Nevertheless, the basis set construction procedure presented here is applicable to DFT calculations as well as to wavefunction based methods.

Section II gives the essential details of the problem and reviews our previous basis set construction procedure.[23] We single out the points that should be kept in the new procedure and discern principles and requirements that were omitted. Subsection III A details the basis set construction for the hydrogen iso-electronic sequence in an arbitrary B field. From the newly constructed one-electron system basis set, in Subsection III B we extend the treatment to multi-electron atoms or atomic ions by modification to recognize orbital occupations. The result is a set of formulae for constructing basis sets for multi-electron atomic systems in a B field. In Sec. IV, we summarize and make a few conclusions.

II. METHODOLOGY

A. Basics

The system Hamiltonian of a central field atom at the origin in a uniform, static external magnetic field along the z direction, $\mathbf{B} = B\hat{z}$, commutes with rotations about $\hat{z}$, so the total magnetic quantum number $\sum_i m_i$ of all electrons remains good, where m_i is the magnetic quantum number for the ith electron. The total spin $\mathbf{S}^2$, its z component S_z, and spatial parity in z also are conserved, so a state can be labeled by those quantum numbers. We choose the Coulomb gauge, $\mathbf{A}(\mathbf{r}) = \frac{1}{2}\mathbf{B} \times \mathbf{r}$, with $\mathbf{A}$ as the vector potential. Then the system Hamiltonian is

$$H = \sum_i \left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + \frac{B^2}{8}\left(x_i^2 + y_i^2\right) + \frac{B}{2}\left(m_i + 2m_{s,i}\right) \right] + \frac{1}{2}\sum_{i \neq j} \frac{1}{\left|\mathbf{r}_i - \mathbf{r}_j\right|}, \tag{1}$$

with $\mathbf{r}_i$ and $m_{s,i}$ as the space coordinate and spin z component for the ith electron. [Hartree atomic units ($\hbar = m_{electron} = q_{electron} = 1$) are used throughout unless otherwise noted. One Hartree a.u. of magnetic field equals 2.3505×10^5 T.] In what follows, unpaired electrons are always taken as spin down, $m_{s,i} = -\frac{1}{2}$, unless stated otherwise.

B. Previous construction scheme

In cylindrical coordinates (ρ, z, ϕ), the jth AGTO basis function takes the form

$$\chi_j(\rho, z, \phi) = N_j \rho^{n_{\rho_j}} z^{n_{z_j}} e^{-\alpha_j \rho^2 - \beta_j z^2} e^{i m_j \phi}, j = 1, 2, 3, \ldots, \tag{2}$$

where $n_{\rho_j} = |m_j| + 2k_j, k_j = 0, 1, \ldots$, with $m_j = \ldots, -2, -1, 0, 1, 2, \ldots$, and $n_{z_j} = \pi_{z_j} + 2l_j, l_j = 0, 1, \ldots$, with $\pi_{z_j} = 0, 1$. Such functions are advantageous for the study of atoms in strong B fields because of their flexibility in describing the elongation of the electron orbitals and densities along the B field direction. Since the B field compresses the transverse (radial) functions (related to exponents α_j) relative to the corresponding longitudinal (axial) ones (exponents β_j), we always have $\alpha_j \geq \beta_j$. Schmelcher and Cederbaum deduced all the required matrix elements of the Hamiltonian with respect to such AGTO basis functions.[15] However, the optimal determination of the sets $\{\alpha_j\}$ and $\{\beta_j\}$ was left largely as an open question.

As previously mentioned, we constructed KL-like highly optimized basis sets without requiring case-by-case full nonlinear optimization.[23] We summarize that procedure to lay the ground work for the new scheme.

A very highly accurate total energy for the non-relativistic H atom at $B = 0$ a.u. is given by an even-tempered Gaussian (ETG) sequence of length N_b and rule of formation,[26]

$$\begin{aligned} \beta_j &= pq^j, \; j = 1, 2, \ldots, N_b, \\ \ln p &= a \ln(q-1) + a', \\ \ln(\ln q) &= b \ln N_b + b', \\ a &= 0.3243, \quad a' = -3.6920, \\ b &= -0.4250, \quad b' = 0.9280, \end{aligned} \tag{3}$$

with $N_b = 16$. This determines the parameters p and q, hence the longitudinal exponents β_j, of what we choose as the "base sequence," that is, the exponent set with reference to which all the others are constructed.

First, since the magnetic field does not change the confinement along z, we expect little effect of B upon the ETG exponents. Therefore our construction retained the ETG sequence Eq. (3) unchanged for the longitudinal exponents β_j. The one modification occurs in cases for which the electron density has diffuse, non-zero orbital angular momentum contributions. Those require that the tempering be extrapolated to include a small number of negative j values.

Then, by consideration of large and small B field limits and use of a nonlinear fit to calculated one-electron system results, Ref. 23 reached a prescription for highly refined, nearly optimal exponents for Eq. (2). Those AGTO basis sets are comprised of one to five exponent sequences ($\ell = 1, 2, 3, 4, 5$), Each sequence is a subset of exponents related by

$$\alpha_{j,\ell} = \beta_j + (1 + \mu_\ell)\Delta(B), \tag{4}$$

$$\mu_1 = 0.0\ , \ \mu_{2,3} = \pm 0.2\ , \ \mu_{4,5} = \pm 0.4\ , \tag{5}$$

and

$$\Delta(B) = \frac{B}{20}\left\{4\left[1 + \frac{4}{b(\gamma)}\frac{\beta_j}{B}\right]^{-2} + \left[1 + \frac{4}{b(\gamma)}\frac{\beta_j}{B}\right]^{-1/2}\right\}, \tag{6}$$

where

$$b(\gamma) = -0.16[\tan^{-1}(\gamma)]^2 + 0.77\tan^{-1}(\gamma) + 0.74\ , \tag{7}$$

$$\gamma = B/Z^2\ . \tag{8}$$

The initial sequence for these exponents is $\mu_{\ell=1} = 0$. Then $\mu_\ell = \pm 0.2$ and ± 0.4 for the second, third, fourth, and fifth sequences, respectively. For $\ell = 2, 3$, there are half as many exponents (with doubled spacing) as in the base sequence, while for $\ell = 4, 5$, there are one-fourth as many (with quadrupled spacing).

Testing showed that the resulting basis sets, Eqs. (4)–(8), introduce errors of less than 1 μhartree for the H atom over $0 \leq B \leq 2000$ a.u. as compared with more accurate algebraic results.[3] Further, the HF total energies for multi-electron atoms from the AGTO prescription, Eqs. (4)–(7), are nearly indistinguishable from full numerical two-dimensional mesh results.[4]

However, our previous scheme has several limitations. First, the scheme makes no distinction among orbitals of different types (different quantum numbers), yet clearly the physics of magnetic confinement is not identical. Second, no consideration of the strong electron-electron interaction in a multi-electron system was involved. Finally, up to five sequences from Eq. (5) were required to reach appropriate accuracy. Including multiple sequences may offset, in part at least, the aforementioned two deficiencies in the constructed basis sets. But as already noted, multiple sequences introduce unfavorable computational cost scaling, especially for highly correlated methods applied to many-electron systems. Thus the endeavor here is to include as few sequences as possible in our basis sets, ideally only one.

One other aspect of our previous basis set construction scheme is worth mentioning because it is important enough that we retained it. This is a pair of constraints on $\Delta(B)$ for very small and very large longitudinal basis set exponents. Specifically, we take $\Delta(B) = \frac{B}{4}$ in the limit $\beta_j \to 0$. This can be viewed as the large B limit or the zero nuclear charge limit. Either way, the one-electron state is a Landau orbital, with an exponential parameter $\alpha_j \equiv a_B = B/4$ (a_B is the scale parameter in the Landau orbital). The opposite limit, $\beta_j \to \infty$, corresponds to $B = 0$ a.u. which restores spherical symmetry, $\alpha_j = \beta_j$, hence $\Delta(B = 0) = 0$. We found that a convenient choice for orbital exponent asphericity is a scaling of a_B. Then $\Delta(B)$ is taken as a monotonically decreasing function of the increasing longitudinal exponents β_j of the functions in a given basis set. The underlying physics is that a small-exponent basis function samples a large volume far from the nucleus. In that region, the B field far outweighs the nuclear attraction, with the consequence that the distortion (relative to the field-free spherical symmetry) will be relatively larger than for the region sampled by larger-exponent basis functions.

III. NEW CONSTRUCTION SCHEME

Extension of Eqs. (4)–(7) is required to allow better fitting to the numerically optimized transverse exponents. But this must be done with a concurrent goal of simplification, namely, getting rid of the multiple sequences. Substantial numerical experimentation and testing of several plausible expressions was required to arrive at expressions that seem superior because of their combined simplicity, accuracy, and flexibility. The easiest way to understand the rationale is to recognize that the construction has two phases, one-electron and multi-electron. Subsections III A and III B present those.

A. Basis sets for hydrogen atom and hydrogen-like ions in *B* field

Since there is only one electron in the hydrogen isoelectronic sequence, electron-electron interaction disappears in these paradigmatic systems. The first step is to optimize transverse exponents α_j. Unlike our previous study, in which we optimized α_j by starting from the spherical base sequence ($\alpha_j = \beta_j$), Eq. (3), and used a down-hill algorithm,[23] in this study we started from a base sequence generated by Eq. (6). Simply because of its explicit asphericity, it undoubtedly is an improved starting point. Then we employed conjugate gradient algorithm searching in the parameter space $\{\alpha_j\}$ to minimize the total energy of the system. That produces both faster and more reliable numerical convergence.[27]

The transverse exponent α_j optimization was done for the H iso-electronic series (H, He$^+$, Li^{++}, Be^{+++}, B^{4+}, C^{5+}, N^{6+}, and O^{7+}) in reduced fields $\gamma = 0.1$, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000. Our previous scheme fits only to optimized α_j's for the 1*s* orbital ($m = \pi_z = 0$), and we applied the resulting expression, Eq. (6), to other orbitals as well. Closer examination, however, shows differences among orbitals which must be taken into account if a truly highly accurate basis is to be had. An example of the orbital dependence is shown in Fig. 1. It displays the results of optimization for $\gamma = 1$ for three different orbitals, namely, 1*s*, 2p_{-1}, and 3d_{-2}. Note the asphericity of the basis function as measured by $(\alpha_j - \beta_j)/B$, which is the vertical axis in that plot. Several observations ensue from examining Fig. 1.

First, the data points of a given orbital with different nuclear charges but for fixed γ fall on the same curve. For example, all the black symbols are for 1*s* orbitals, but the nuclear charge *Z* ranges from 1 (neutral H) to 8 (O^{7+}), yet obviously they all lie on a single curve. A simple argument shows that this must be the case. This apparently was first shown by Surmelian and O'Connell.[28] Also see the work of Ruder *et al.*[29] Suppose the H atom wavefunction in an external *B* field is $\Psi_H(\mathbf{r}, B)$, then Eq. (1) gives

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r} + \frac{B^2}{8}\left(x^2+y^2\right) + \frac{B}{2}\left(m+2m_s\right)\right]\Psi_H(\mathbf{r},B) = E_H\Psi_H(\mathbf{r},B).$$

Scaling $\mathbf{r} \to Z\mathbf{r}$ and multiplication by Z^2 gives

$$\left[-\frac{1}{2}\nabla^2 - \frac{Z}{r} + \frac{(Z^2B)^2}{8}\left(x^2+y^2\right) + \frac{Z^2B}{2}\left(m+2m_s\right)\right]\Psi_H(Z\mathbf{r},B) = (Z^2E_H)\Psi_H(Z\mathbf{r},B).$$

The scaled Hamiltonian is the same as that of a hydrogen-like atom with nuclear charge Z in an external field $B' = Z^2B$ or, equivalently, $\gamma = \frac{B'}{Z^2} = B$. The scaled hydrogen-atom wavefunction is precisely the eigenfunction of this Hamiltonian with energy of Z^2E_H. Now we expand $\Psi_H(\mathbf{r}, B)$ in the optimized basis set,

$$\Psi_H(\mathbf{r},B) = \sum_j a_j\chi_j = \sum_j a_jN_j\rho^{n_{\rho_j}}z^{n_{z_j}}e^{-\alpha_j\rho^2-\beta_jz^2}e^{im\phi}\,. \tag{9}$$

The scaled wavefunction accordingly is

$$\begin{aligned}\Psi_Z(\mathbf{r},Z^2B) &= \Psi_H(Z\mathbf{r},B)\\ &= \sum_j a_jN_jZ^{n_{\rho_j}+n_{z_j}}\rho^{n_{\rho_j}}z^{n_{z_j}}e^{-\alpha'_j\rho^2-\beta'_jz^2}e^{im\phi},\end{aligned}$$

where $\alpha'_j = Z^2\alpha_j$ and $\beta'_j = Z^2\beta_j$. Obviously, $\frac{\alpha'_j-\beta'_j}{B'} = \frac{\alpha_j-\beta_j}{B}$ and $\frac{\beta'_j}{B'} = \frac{\beta_j}{B}$, which shows that the two cases indeed are on the same curve.

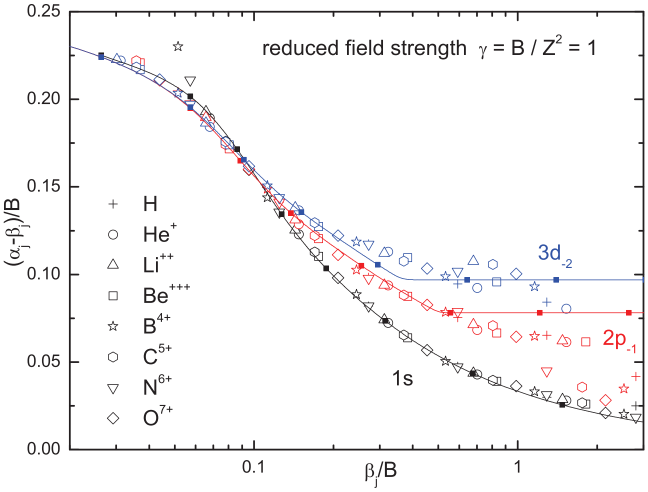

FIG. 1. Fitting the optimized exponents of AGTO basis functions for hydrogen atom and hydrogen-like ions in reduced magnetic field strength $\gamma = 1$. Empty symbols are optimized exponents from searching $\{\alpha_j\}$ space. Solid curves are fits to those data points, generated by Eqs. (10)–(13). Filled squares are the AGTO basis sets for the hydrogen atom in $B = 1$ a.u. generated according to Eqs. (10)–(15). Black, red, and blue stand for the 1*s*, 2p_{-1}, and 3d_{-2} orbitals, respectively.

Second, though the optimized data points for orbitals with different quantum numbers do not fall on the same curve, their trends as functions of *B* are similar. To accommodate this behavior, we introduce two parameters that depend upon the reduced field strength and orbital quantum numbers, $A(\gamma, m, \pi_z)$ and $D(\gamma, m, \pi_z)$. Their purpose is to provide orbital-dependent asphericity in the basis functions. After extensive numerical exploration, we reached a prescription for the orbital-dependent version of Δ, namely,

$$\Delta_j(\beta_j,B) = B\left\{\left(\frac{1}{4}-\frac{\beta_j}{B}\right)\left[1-\left(1-e^{-30\beta_j/B}\right)^8\right] + \frac{A(\gamma,m,\pi_z)}{(\beta_j/B)^{D(\gamma,m,\pi_z)}}\left(1-e^{-30\beta_j/B}\right)^8\right\}. \tag{10}$$

Initially, the parameters $A(\gamma, m, \pi_z)$ and $D(\gamma, m, \pi_z)$ were obtained from fits to the data points such as those displayed in Fig. 1 by use of Eq. (10) for each $\gamma = 0.1$, 0.2, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, 1000 and for each of five orbitals, 1*s*, 2p_0, 2p_{-1}, 3d_{-1}, and 3d_{-2}. With that set of parameters $A(\gamma, m, \pi_z)$ and $D(\gamma, m, \pi_z)$ determined, a second fit was made to express those parameters as analytical functions of reduced field strength γ and orbital quantum numbers *m* and π_z. The final result is

$$\begin{aligned}D(\gamma,m,\pi_z) &= 0.4 + \frac{0.6(l+1)/(l^2+l+1)}{1+1.105(l+1)^3\gamma^{0.425(l+2)}},\\ A(\gamma,m,\pi_z) &= \frac{0.020\,73+0.000\,35(2\pi_z+l(l-1)/3)}{D(\gamma,m,\pi_z)^{1.25}},\end{aligned} \tag{11}$$

where $l = |m| + \pi_z$.

The final observation is specific to the H iso-electronic series. As one sees in Fig. 1, except for the 1*s* orbital, the asphericity of basis functions does not vanish for very tight functions when $\beta_j \to \infty$. Instead the higher orbital asphericities go to some non-zero, nearly constant values. This behavior is understandable from decomposition of the wavefunction into radial and angular parts. The kinetic energy operator in the Hamiltonian Eq. (1) acting on the angular part of the wavefunction gives rise to a repulsive centrifugal potential for the non-zero angular momentum orbitals. That kills the singularity in the nuclear attractive potential. Thus, the overpowering Coulomb attraction exists only for the *s* orbital for very tight functions, for which the asphericity of *s* basis functions, $(\alpha_j - \beta_j)/B$, does go to zero when $\beta_j \to \infty$. For non-zero angular momentum orbitals, the strong repulsive centrifugal potential causes the coefficients a_j in the wavefunction expansion, Eq. (9), to become negligible quickly with increasing β_j (tighter and tighter basis functions). Thus it is useful and effective to use a cutoff as a simple approximation to the limit of $\Delta_j(B)$ as $\beta_j \to \infty$. We impose a minimum value for $\Delta_j(B)$ according to

$$\Delta_{\min}(B) = \begin{cases} 0, & \text{if } m = \pi_z = 0, \\ \dfrac{0.1562B}{1+\gamma^{-0.55}}, & \text{if } |m| = 1 \text{ and } \pi_z = 0, \\ \dfrac{0.1744B}{1+0.8\gamma^{-0.55}}, & \text{otherwise.} \end{cases} \tag{12}$$

Combining Eqs. (10) and (12) yields the highly optimized transverse exponents α_j of the AGTO basis functions for the hydrogen iso-electronic sequence in an arbitrary B field,

$$\alpha_j = \beta_j + \max(\Delta_j(\beta_j, B), \Delta_{\min}(B)). \tag{13}$$

To this point, we have only explored the parameter space $\{\alpha_j\}$ with $\{\beta_j\}$ kept unchanged as in the base ETG sequence; see Eq. (3). This strategy is not entirely advantageous because the basis functions which have intermediate asphericity ($0.05B \lesssim \alpha_j - \beta_j \lesssim 0.20B$) may not be adequate in number. Thus we require the asphericities of any two adjacent basis functions, say the *j*th and $(j+1)$th, to differ by no more than $0.03B$. This is a heuristic choice which seems to be well balanced. Its practical effect is evident. For any AGTO basis function $0 \le \alpha_j - \beta_j \le 0.25B$, setting the maximum interval at $0.03B$ results in there being at least $\frac{0.25}{0.03} \approx 8$ basis functions included for the range over which the asphericity changes from zero to its maximum value, 0.25. That is, we use a denser set of basis functions in the exponent range through which the basis function asphericity changes most rapidly. To avoid approximate linear dependencies from excessively dense spacing of functions, we also require that the ratio of the longitudinal exponents of any two adjacent basis functions be no less than $\sqrt{q}$, where q is from Eq. (3). This is a modification of that equation. At the ratio $\sqrt{q}$, there is twice the basis function density than from use of the ratio q. Heuristically this works well in avoiding approximate linear dependencies while handling changing asphericity. To enforce those constraints, first we need the inverse of Eq. (10),

$$\beta_j = \Delta_j^{-1}\left(\Delta_j(\beta_j, B), B\right). \tag{14}$$

Then the recursive relations for determination of β_j are

$$\begin{aligned} \beta_{j+1} &= \min\left(\max\left(\Delta_{j+1}^{-1}\left(\alpha_j - \beta_j - 0.03B, B\right), \sqrt{q}\beta_j\right), q\beta_j\right), \\ \beta_{j-1} &= \max\left(\min\left(\Delta_{j-1}^{-1}\left(\alpha_j - \beta_j + 0.03B, B\right), \beta_j/\sqrt{q}\right), \beta_j/q\right), \\ \beta_0 &= p, \end{aligned} \tag{15}$$

where p and q are defined in Eq. (3). This completes the AGTO basis set construction for the hydrogen iso-electronic sequence in an external constant B field.

To see how faithfully the new prescription reproduces the fully optimized exponents, as shown in Fig. 1 with empty symbols, the three solid curves in the figure follow from Eqs. (10)–(13). Indeed, the fits are excellent except in the regions of very tight functions for orbitals with non-zero angular momentum, where we adopted the simplified cutoff. Because that is in the weak field regime, in practice, the deviation does not pose any serious problem. See the discussion above [Eq. (12)]. The AGTO basis sets for the three orbitals, 1*s*, $2p_{-1}$, and $3d_{-2}$, for the hydrogen atom in $B = 1$ a.u., generated according to our construction, Eqs. (10)–(15), are represented in the figure by filled symbols. Using those three newly constructed AGTO basis sets, we obtain atomic energies of −0.831 168 2 hartree, −0.456 596 1 hartree, and −0.353 047 1 hartree. Comparison with the presumably more accurate algebraic results by Kravchenko *et al.*[3] (−0.831 168 896 733 hartree, −0.456 597 058 424 hartree, and −0.353 048 025 149 hartree) gives residual errors from our AGTO scheme as less than 1 μhartree.

More test results are included in Tables I and II. We can see that the absolute error from our constructed AGTO basis set ranges from a fraction of 1 μhartree to a few μhartrees. While the absolute error increases with increasing B field strength, the relative error does not. The mean absolute errors (MAEs) of the seven states included in Table II range from 1.4 μhartree to 4.2 μhartree. It is especially noteworthy that not all of those states were used in the optimization of exponents nor in the fitting. The accuracy of our present basis sets which include only a single sequence surpasses that of our previous basis sets, Eqs. (5)–(7), in which double sequences were included. Indeed the accuracy of the new sets is nearly on par with previous basis sets that used triple sequences.

Considering the substantially reduced size of the new hydrogenic AGTO basis sets, we turn in Subsection III B to the problem of extending that improvement to many-electron atoms in a strong B field.

B. Basis sets for many-electron atoms and ions in *B* field

There are several complications due to the electron-electron interaction in a many-electron atom or ion. If the 1*s* orbital is occupied by one or two electrons, the singular nuclear attractive potential will be screened and hence be less effective in driving down the asphericity of tight basis functions in orbitals other than 1*s* than is the case for hydrogen-like ions. This effect dwindles for more diffuse basis functions; hence, it may be neglected beyond some point in a sequence of increasingly diffuse exponents. Evidently the effect is inversely proportional to the average distance between the orbital and the nucleus, which is related to the quantum numbers m and π_z of the orbital. On the other hand, outer electrons also affect 1*s*

TABLE I. Comparison of the H atomic energies in **B** fields between our present study using a single sequence of AGTO basis functions and the more accurate algebraic results as reference values. (Atomic energies are in hartree, absolute errors are in μhartree, relative errors are in millionth, and **B** is in a.u.)

	H (1s)				H ($2p_0$)			
B (a.u.)	Present	Ref.[a]	Error (μhartree)	Relative error	Present	Ref.[a]	Error (μhartree)	Relative error
0	−0.499 999 93	−0.500 000 00	0.07	0.14	−0.124 999 88	−0.125 000 00	0.12	1.0
0.01	−0.504 974 93	−0.504 975 00	0.07	0.14	−0.129 850 22	−0.129 850 42	0.20	1.5
0.02	−0.509 899 98	−0.509 900 04	0.06	0.14	−0.134 406 04	−0.134 406 47	0.43	3.2
0.05	−0.524 376 64	−0.524 376 71	0.07	0.13	−0.146 463 26	−0.146 464 84	1.6	10.8
0.1	−0.547 526 39	−0.547 526 48	0.09	0.17	−0.162 408 20	−0.162 410 08	1.9	11.5
0.2	−0.590 381 38	−0.590 381 57	0.19	0.31	−0.185 182 48	−0.185 184 04	1.6	8.5
0.5	−0.697 210 07	−0.697 210 54	0.47	0.7	−0.224 759 3	−0.224 760 34	1.0	4.5
1	−0.831 168 21	−0.831 168 90	0.69	0.8	−0.260 004 1	−0.260 006 62	2.5	9.7
2	−1.022 212 4	−1.022 213 91	1.5	1.5	−0.297 709 1	−0.297 710 97	1.9	6.2
5	−1.380 397 5	−1.380 398 87	1.4	1.0	−0.347 616 4	−0.347 617 78	1.3	3.8
10	−1.747 796 2	−1.747 797 16	0.9	0.5	−0.382 647 4	−0.382 649 85	2.4	6.4
20	−2.215 396 7	−2.215 398 52	1.8	0.8	−0.413 374 3	−0.413 377 73	3.4	8.3
50	−3.017 857 2	−3.017 860 71	3.6	1.2	−0.445 682 6	−0.445 685 11	2.5	5.6
100	−3.789 797 7	−3.789 804 24	6.5	1.7	−0.463 616 5	−0.463 617 76	1.3	2.8
200	−4.727 140 9	−4.727 145 11	4.2	0.9	−0.476 531 3	−0.476 532 00	0.7	1.5
500	−6.257 081 6	−6.257 087 67	6.0	1.0	−0.487 506 9	−0.487 507 10	0.2	0.5
1000	−7.662 415 4	−7.662 423 25	7.8	1.0	−0.492 494 8	−0.492 495 00	0.2	0.4
2000	−9.304 755 7	−9.304 765 08	9.4	1.0				
4000	−11.204 134 0	−11.204 145 21	11.2	1.0				

	H ($2p_{-1}$)				H ($3d_{-2}$)			
B (a.u.)	Present	Ref.[a]	Error (μhartree)	Relative error	Present	Ref.[a]	Error (μhartree)	Relative error
0	−0.124 999 88	−0.125 000 00	0.12	1.0	−0.055 555 11	−0.055 555 56	0.45	8.0
0.01	−0.134 701 01	−0.134 701 14	0.13	1.0	−0.069 246 69	−0.069 247 18	0.49	7.2
0.02	−0.143 817 41	−0.143 817 61	0.20	1.4	−0.080 685 15	−0.080 685 87	0.72	8.9
0.05	−0.168 057 83	−0.168 058 19	0.36	2.2	−0.106 888 68	−0.106 888 75	0.07	0.7
0.1	−0.200 845 44	−0.200 845 67	0.23	1.2	−0.137 838 95	−0.137 839 52	0.57	4.1
0.2	−0.250 538 86	−0.250 539 10	0.24	0.9	−0.181 320 01	−0.181 320 61	0.60	3.3
0.5	−0.349 476 68	−0.349 477 30	0.62	1.8	−0.264 389 27	−0.264 389 55	0.28	1.1
1	−0.456 596 14	−0.456 597 06	0.92	2.0	−0.353 047 15	−0.353 048 03	0.88	2.5
2	−0.599 611 93	−0.599 612 77	0.84	1.4	−0.471 170 4	−0.471 171 93	1.5	3.2
5	−0.859 831 70	−0.859 832 62	0.92	1.1	−0.686 799 4	−0.686 802 52	3.1	4.5
10	−1.125 420 6	−1.125 422 34	1.7	1.5	−0.908 211 7	−0.908 214 78	3.1	3.4
20	−1.465 503 7	−1.465 508 55	4.8	3.3	−1.193 627 4	−1.193 633 18	5.8	4.9
50	−2.056 842 2	−2.056 846 67	4.5	2.2	−1.694 314 6	−1.694 321 25	6.7	3.9
100	−2.634 753 3	−2.634 760 67	7.4	2.8	−2.188 163 8	−2.188 167 24	3.5	1.6
200	−3.347 136 0	−3.347 145 23	9.3	2.8	−2.801 995 8	−2.802 000 03	4.3	1.5
500	−4.531 236 8	−4.531 246 38	9.6	2.1	−3.832 385 5	−3.832 390 06	4.5	1.2
1000	−5.638 409 7	−5.638 421 08	11.4	2.0	−4.805 105 7	−4.805 110 67	5.0	1.0

[a] Data are from Ref. 3.

electron(s). Among them, the innermost (tightly bound) non-$1s$ orbital ($m \neq 0$, $\pi_z = 0$) dominates, so it is the only one that we consider here. If the $1s$ orbital is doubly occupied, of course the two $1s$ electrons are strongly repulsive to each other, a fact we also shall take into account.

To describe the aforementioned effects, we generalize Eq. (13) to become

$$\alpha_j = \beta_j + f(\beta_j, m_j, \pi_j, B)\Delta_j(\beta_j, B) \ . \tag{16}$$

The new feature is the rescaling factor f,

$$f(\beta_j, m_j, \pi_j, B) = \begin{cases} 1 - \dfrac{N_{1s}}{20}, & \text{if } |m_j| + \pi_j > 0, \text{ and } \Delta_j = \alpha_j - \beta_j < \dfrac{0.14(\pi_j + 1.2|m_j|)B}{\pi_j + |m_j|}, \\ 1 - \dfrac{1}{20|m_t|}, & \text{if } |m_j| = \pi_j = 0, m_t \neq 0, \text{and } \Delta_j = \alpha_j - \beta_j < 0.17B, \\ 1 - \dfrac{N_{1s} - 1}{20}, & \text{if } |m_j| = \pi_j = 0, N_{1s} > 1, \text{and } \Delta_j = \alpha_j - \beta_j < 0.17B, \\ 1, & \text{otherwise} \ , \end{cases} \tag{17}$$

TABLE II. Basis set errors for the H atom in **B** fields.[a] (Absolute errors are in μhartree, numbers in parentheses are the relative errors in millionths, and **B** is in a.u.)

B (a.u.)	1s	$2p_0$	$2p_{-1}$	$3d_{-1}$	$3d_{-2}$	$4f_{-3}$	$5g_{-4}$
0	0.1(0.1)	0.1(1.0)	0.1(1.0)	0.4(8.0)	0.4(8.0)	0.7(24)	2.0(99)
0.01	0.1(0.1)	0.2(1.5)	0.1(1.0)	0.9(14)	0.5(7.2)	1.1(23)	1.7(45)
0.02	0.1(0.1)	0.4(3.2)	0.2(1.4)	1.7(23)	0.7(8.9)	0.5(7.9)	0.9(19)
0.05	0.1(0.1)	1.6(11)	0.4(2.2)	0.4(4.8)	0.1(0.7)	0.2(2.2)	−0.1(1.8)
0.1	0.1(0.2)	1.9(12)	0.2(1.2)	0.2(1.8)	0.6(4.1)	1.1(9.9)	0.4(3.9)
0.2	0.2(0.3)	1.6(8.5)	0.2(0.9)	0.2(1.9)	0.6(3.3)	0.7(4.6)	1.0(7.7)
0.5	0.5(0.7)	1.0(4.5)	0.6(1.8)	2.1(12)	0.3(1.1)	1.1(4.7)	6.3(32)
1	0.7(0.8)	2.5(9.7)	0.9(2.0)	3.2(15)	0.9(2.5)	2.3(7.8)	7.7(29)
2	1.5(1.5)	1.9(6.2)	0.8(1.4)	2.5(10)	1.5(3.2)	3.3(8.3)	8.0(22)
5	1.4(1.0)	1.3(3.8)	0.9(1.1)	6.7(23)	3.1(4.5)	4.7(7.9)	4.8(9.1)
10	0.9(0.5)	2.4(6.4)	1.7(1.5)	6.8(20)	3.1(3.4)	4.0(5.0)	2.5(3.5)
20	1.8(0.8)	3.4(8.3)	4.8(3.3)	7.6(20)	5.8(4.9)	7.2(6.9)	3.0(3.2)
50	3.6(1.2)	2.5(5.6)	4.5(2.2)	4.7(11)	6.7(3.9)	7.3(4.9)	4.2(3.1)
100	6.5(1.7)	1.3(2.8)	7.4(2.8)	2.9(6.4)	3.5(1.6)	4.5(2.3)	9.2(5.3)
200	4.2(0.9)	0.7(1.5)	9.3(2.8)	1.5(3.2)	4.3(1.5)	5.3(2.1)	5.9(2.6)
500	6.0(1.0)	0.2(0.5)	9.6(2.1)	0.5(1.1)	4.5(1.2)	6.1(1.8)	7.1(2.3)
1000	7.8(1.0)	0.2(0.4)	11.4(2.0)	0.1(0.2)	5.0(1.0)	6.4(1.5)	7.4(1.9)
MAE	2.09(0.7)	1.36(5.1)	3.12(1.8)	2.49(10)	2.45(3.6)	3.32(7.3)	4.24(17)

[a] Reference values used to deduce basis set errors are from Ref. 3 for the $1s$, $2p_0$, $2p_{-1}$, $3d_{-1}$, and $3d_{-2}$ states. For the states $4f_{-3}$ and $5g_{-4}$, reference data are taken from our calculation with very large basis sets which include multiple sequences (through five) of Eq. (5). There is slight improvement over our earlier published results in the low-B field region.[23]

where $N_{1s} \in [0, 2]$ is the number of electrons that occupy the $1s$ orbital, including the spin-up and the spin-down electrons, and m_t is the magnetic quantum number of the occupied innermost tightly bound orbital for which the z-parity is even. Observe that Eqs. (15) remain valid since only the transverse part of the function is modified. What Eq. (17) does is reduce the asphericity slightly at fixed B. That would lead to moving the points from the upper members of the iso-electronic sequence slightly downward in the right two-thirds of a many-electron version of Fig. 1. The shift is not enough to warrant a separate figure. There is a welcome feature of the $1s$ orbital being occupied. Since the nucleus is now screened by the innermost electron cloud, the effective repulsive centrifugal potential for non-zero angular momentum orbitals also is smoothed and a cutoff, Eq. (12), no longer is required.

Lastly, consider the situation in which more than one shell of a single kind of orbital is occupied, for example, the $1s2s$ configuration for the He atom and the ground state $1s^2 2s$ for the Li atom in a weak B field. Although we have tried to optimize the transverse exponents by exploring the $\{\alpha_j\}$ space while keeping only a single sequence, unfortunately we did not succeed in getting adequately accurate basis sets. The difficulty can be traced to the quite different behaviors of $1s$ and $2s$ orbitals. It seems unavoidable to have a second basis function sequence. As we observed above, the severest demands upon basis functions are for those having intermediate asphericities. Bearing this in mind, we choose to limit the second sequence of basis functions to have asphericity between $0.03B$ and $0.225B$. Again this is a design choice which is based on the fact that the asphericity curves in Fig. 1 are rather flat in the ranges 0–$0.03B$ and $0.225B$–$0.25B$. Use of a larger range would result in excessively many basis functions in the second sequence and hence an un-necessary increase of the basis set size. For small B, the basis functions in the second sequence may collapse into (i.e., be approximately linearly dependent with) the first sequence. To avoid this problem, a minimum B field strength of 0.2 a.u. is effective as a parameter in calculating $\Delta_j(\beta_j, B)$ for the second sequence. Thus the second sequence is generated according to

$$\begin{aligned} \alpha_{j,2} &= \beta_j + 0.8\Delta_j(\beta_j, \max(B, 0.2)), \\ &\text{if } 0.03B < \Delta_j(\beta_j, B) < 0.225B. \end{aligned} \tag{18}$$

Another technique to avoid basis function collapse is to use $k_j = 1$, (e.g., $n_{\rho_j} = |m_j| + 2k_j = |m_j| + 2$) for the basis functions, Eq. (2), in the second sequence whenever $\frac{\alpha_j - \beta_j}{\alpha_j + \beta_j} \le 0.05$.

Again because of inner electron screening, each electron in the atom or the ion feels different effective charges, thus different reduced B field strength γ. A detailed analysis can be quite complicated. Instead, we adopt a rough but effective approximation that works quite well. Each electron is assigned an effective nuclear charge Z_{eff}. For the innermost electrons, Z_{eff} should be close to the bare nuclear charge, so we simply take $Z_{eff} = Z$. For other electrons, Z_{eff} is close to the nuclear charge reduced by the number of inner-shell electrons. Hence, the reduced field strengths $\gamma = B/Z_{eff}^2$ are different for each electron. Those values are used for γ that appears in Eqs. (10) and (11). However, notice that the B field experienced by all electrons is the same.

To this point we have not specified the range of the index j in Eq. (2), which determines the number of the basis functions in a basis set. The usual computational practice is to use a range large enough to ensure that the accuracy of the basis set is not degraded by insufficient tight functions or diffuse functions. More precisely, the incremental error introduced into the basis set by removing the most diffuse or the most tight basis function should not exceed the residual error in the unaltered basis set. This criterion can be met with little difficulty in practice simply by repeatedly removing the most diffuse or the most tight basis function and checking the calculated results. We did tabulate the ranges for different B field strengths and different orbitals in our computer code but do not dwell on it here because the results are both quite straightforward and not very informative. One caveat is that in the cases for which the electron density has diffuse, nonzero orbital angular momentum contributions, sometimes it is necessary to extrapolate to negative j values and to include a small number of such diffuse basis functions in the basis sets.

We note that many constants which appear in Eqs. (10)–(18) are either chosen by physical plausibility or were determined by fitting to numerically optimized data points followed by fine tuning to achieve the best overall performance. When the results proved comparatively insensitive to a constant, we chose a simpler value to keep the expressions concise. The forms of these equations are devised in the hope of encapsulating most of the underlying physics.

We use published HF calculations for atoms in strong B fields to assess the accuracy of our newly constructed basis sets. The basis set errors are given in Tables III–VII for atoms He through C and a few ions. In all cases, the electronic states are labeled according to their corresponding zero field HF electronic configurations. We did not include correlated wavefunction or DFT calculations because we focus only on basis set construction in this study, and calculations including electron correlation would complicate our comparisons. However, we note that the basis sets constructed according to the new procedure are intended for use both in correlated wavefunction and DFT calculations, not just HF calculations.

There is an issue of reference data. For the He atom, Ruder and co-workers did extensive HF calculations and gave abundant tabulated data.[29] Jones, Ortiz, and Ceperley also used AGTO basis functions but different basis sets.[8] Zhao and Stancil used a B-spline basis and quadruple-precision calculations to obtain very accurate HF energies for $0 \leq B \leq 100$ a.u., but their data are only available for the $1s^2$ state.[7] Using different sources as reference data will introduce non-uniformity of accuracies, thus jeopardize clarity of comparison. Hence, we decided to use our own recent results as reference. They were obtained by using the multiple sequence AGTO basis functions.[23] They were in good agreement with other published results and even have higher accuracy for some states (lower HF energies compared to Ref. 8).

Basis set errors for the He atom in B fields are shown in Table III. Absolute errors range from a few to a couple of hundreds of μhartree, with an average of a few tens of μhartree. Understandably they are larger than the basis set errors for H atom, but the relative errors are not. The MAE for the $1s2s$ state seems significantly smaller than those of other states, simply because double sequences were employed for that case alone. At low field strength $B = 0.1$ a.u., there are several negative values in the table, which means that our current single sequence basis sets give lower HF energies than the reference calculations that used the multiple sequence basis sets of Eq. (5). The improvement is obvious. The test on this simplest two-electron system shows that our constructed basis sets work as well for these systems as they do for a single-electron system, H atom.

Tables IV–VII give the basis set errors for the Li, Be, B, and C atoms and the positive ions, Li^+, Be^+, and B^+, in field strengths $0 \leq B \leq 2000$ a.u. Comparison data for atoms and ions with $Z \geq 3$ are from the series studies by Ivanov and Schmelcher, who used two-dimensional (2D) mesh methods.[4] Exceptions are the $1s^2 2s^2$ state of the Be atom and B^+ ion and the $1s^2 2s^2 2p_{-1}$ state of the B atom, for which they allowed asymmetrical wavefunctions for $2s^2$ electrons with respect to the $z = 0$ plane,[4] whereas we required definite z parity, $\pi_z = 0, 1$.

TABLE III. Basis set errors for the He atom in **B** fields.[a] (Absolute errors are in μhartree, numbers in parentheses are the relative errors in millionths, and **B** is in a.u.)

B (a.u.)	$1s^2$	$1s2s$	$1s2p_0$	$1s2p_{-1}$	$1s3d_{-1}$	$1s3d_{-2}$	$1s4f_{-2}$	$1s4f_{-3}$	$1s5g_{-3}$
0	−1(0.3)	1(0.4)	20(9.3)	5(2.4)	0(0.2)	0(0.2)	1(0.5)	0(0.2)	31(15)
0.1	0(0.0)	0(0.0)	25(11)	8(3.7)	−5(2.5)	7(3.4)	−8(3.9)	−13(5.9)	−27(13)
0.2	0(0.1)	4(1.8)	39(17)	19(8.1)	10(4.7)	18(7.9)	7(3.0)	7(3.2)	5(2.1)
0.5	1(0.4)	13(5.2)	53(21)	49(19)	11(4.6)	12(4.8)	7(2.8)	8(3.4)	20(8.5)
1	2(0.6)	11(4.2)	34(13)	61(21)	17(6.6)	18(6.4)	18(7.0)	13(4.9)	46(18)
2	2(1.1)	9(3.0)	27(8.6)	62(18)	19(6.3)	16(4.9)	9(2.9)	19(6.0)	6(2.0)
5	2(4.4)	7(1.8)	11(2.9)	45(9.7)	19(5.0)	17(3.9)	7(1.8)	27(6.6)	1(0.2)
10	20(6.6)	4(0.8)	8(1.7)	29(4.9)	17(3.5)	29(5.5)	8(1.7)	53(10)	3(0.6)
20	17(1.5)	0(0.1)	4(0.6)	38(5.1)	10(1.6)	30(4.4)	4(0.7)	40(6.0)	3(0.5)
50	27(0.7)	−3(0.4)	11(1.3)	65(6.3)	19(2.4)	35(3.7)	9(1.2)	33(3.6)	7(0.8)
100	43(0.5)	0(0.0)	16(1.6)	101(7.7)	20(2.0)	48(4.0)	14(1.4)	36(3.1)	12(1.2)
200	72(0.4)	−6(0.4)	13(1.1)	133(8.0)	16(1.3)	67(4.3)	12(1.0)	46(3.1)	11(0.9)
500	123(0.3)	−4(0.3)	23(1.4)	178(7.9)	11(0.7)	89(4.3)	10(0.6)	62(3.1)	10(0.6)
1000	179(0.2)	−1(0.1)	22(1.1)	204(7.3)	18(0.9)	105(4.0)	17(0.8)	74(3.0)	18(0.9)
2000	189(0.1)	1(0.1)	25(1.0)	220(6.3)	25(1.0)	111(3.4)	24(1.0)	85(2.7)	24(0.9)
MAE	45(1.1)	4(1.2)	22(6.2)	81(9.0)	14(2.9)	40(4.3)	10(2.0)	34(4.3)	15(4.3)

[a] Reference values used to deduce basis set errors are from Ref. 23, in which very large basis sets including multiple sequences of Eq. (5) were used. Recalculation slightly improved over our earlier published results in the low B-field region, $0 \leq B \leq 1$ a.u.

TABLE IV. Basis set errors for the Li singly positive ion and Li atom in **B** fields.[a] (Absolute errors are in mH, numbers in parentheses are the relative errors in millionth, and **B** is in a.u.)

	Li$^+$		Li				
B (a.u.)	$1s^2$	$1s2p_{-1}$	$1s^22s$	$1s^22p_{-1}$	$1s2s2p_{-1}$	$1s2p_02p_{-1}$	$1s2p_{-1}3d_{-2}$
0	0.01(0.8)	0.02(4.3)	0.00(0.1)	0.01(1.7)	0.03(4.7)	0.01(2.4)	0.04(6.9)
0.1	−0.00(0.3)	0.03(5.8)	0.01(1.4)	0.02(3.2)	0.04(7.4)	0.02(3.7)	0.07(13)
0.2	0.00(0.3)	0.03(5.9)	0.00(0.6)	0.03(4.5)	0.11(20)	0.02(3.8)	0.10(18)
0.5	0.00(0.3)	0.04(6.6)	0.01(1.7)	0.05(6.2)	0.03(5.1)	0.06(10)	0.07(11)
1	0.00(0.4)	0.06(10)	0.02(2.1)	0.09(11)	0.05(8.3)	0.15(23)	0.09(14)
2	0.01(1.1)	0.07(10)	0.01(1.1)	0.10(13)	0.11(15)	0.20(27)	0.10(14)
5	0.02(2.7)	0.07(7.7)	0.01(2.3)	0.11(16)	0.01(1.5)	0.19(21)	0.11(12)
10	0.11(36)	0.03(2.9)	−0.07(21)	0.14(30)	0.05(4.2)	0.15(14)	0.10(8.5)
20	0.10(25)	0.04(3.0)	−0.00(0.4)	0.13(74)	0.08(6.1)	0.09(6.1)	0.07(4.6)
50	0.10(3.6)	0.13(7.1)	−0.26(9.3)	0.15(6.1)	0.13(7.0)	0.15(7.7)	0.08(4.0)
100	0.04(0.5)	0.14(6.0)	0.65(9.1)	0.21(3.1)	0.85(35)	0.01(0.4)	0.14(5.4)
200	0.05(0.3)	0.20(6.6)	−0.75(4.5)	0.25(1.6)	0.33(11)	−1.25(40)	0.34(9.7)
500	0.09(0.2)	0.32(7.7)	−1.96(4.3)	0.39(0.9)	3.14(75)	0.83(20)	0.52(11)
1000	0.13(0.1)	0.33(6.2)	12.32(13)	0.74(0.8)	0.92(18)	0.93(18)	0.61(10)
2000	0.23(0.1)	0.36(5.6)	0.00(0.0)	0.94(0.5)	0.33(5.0)	0.43(6.5)	0.66(8.8)
MAE	0.06(4.8)	0.13(6.4)	1.07(4.7)	0.22(12)	0.41(15)	0.30(14)	0.21(10)

[a] Reference values used to deduce basis set errors are from Ref. 4. For B = 2000 a.u., reference data are taken from our calculation with very large basis sets which include multiple sequences of Eq. (5).[23]

For those three instances, the references are taken from our own calculations by using very large basis sets including multiple sequences.[23] We also supplemented the reference data points for the Li atom at B = 2000 a.u.

Basis set errors in these calculations range from a few hundredths to a few mH. As mentioned before, negative values signify that we obtained lower HF energies with our new basis sets than those from our chosen references. Although absolute errors vary a lot, relative errors are not very different from those for the H and He atoms and do not change much with increasing B field strength (except when the total energy of the atom or ion happens to be close to zero) or for different atoms. This is evidence for the uniformity of the quality of our newly constructed basis sets for different atoms in different B field strengths, a welcome feature. Inspection of data in Tables IV–VII shows a few irregularities of error distribution. For example, in the Li atom, the error for the $1s2s2p_{-1}$ state at B = 500 a.u. is 3.14 mH, much larger than the errors at B = 200 a.u. (0.33 mH) and at B = 1000 a.u. (0.92 mH). We surmise that the reason is that our chosen reference data have non-uniform accuracies. Using our own results from multiple sequence calculations,[23] the basis set errors are much more uniform: 0.24 mH, 0.30 mH, 0.28 mH, for B = 200, 500, 1000 a.u., respectively (not included in the table). Another example is the $1s2p_02p_{-1}$ state at B = 200 a.u., for which we got a total HF energy 1.25 mH lower than the reference result. The

TABLE V. Basis set errors for the Be singly positive ion and Be atom in **B** fields.[a] (Absolute errors are in mH, numbers in parentheses are the relative errors in millionths, and **B** is in a.u.)

	Be$^+$			Be			
B (a.u.)	$1s^22s$	$1s^22p_{-1}$	$1s2p_{-1}3d_{-2}$	$1s^22s^2$	$1s^22s2p_{-1}$	$1s^22p_{-1}3d_{-2}$	$1s2p_{-1}3d_{-2}4f_{-3}$
0	0.01(0.6)	0.02(1.1)	0.05(5.8)	−0.00(0.1)	0.03(1.7)	0.04(2.8)	0.08(8.7)
0.5	0.02(1.3)	0.05(3.1)	0.11(10)	0.01(1.0)	0.03(2.1)	0.07(4.7)	0.08(7.5)
1	0.03(2.2)	0.09(6.1)	0.09(7.7)	0.05(3.4)	0.05(3.3)	0.11(7.1)	0.10(8.2)
2	0.05(3.7)	0.13(8.9)	0.10(7.9)	0.07(5.2)	0.06(4.0)	0.18(12)	0.11(8.4)
5	0.05(3.4)	0.18(12)	0.11(7.2)	0.09(10)	0.07(4.7)	0.25(15)	0.18(11)
10	0.03(2.8)	0.16(12)	0.12(6.5)	0.07(44)	0.12(8.7)	0.27(18)	0.14(6.8)
20	0.04(7.0)	0.22(24)	0.11(4.7)	0.07(5.2)	0.12(12)	0.33(30)	0.16(6.2)
50	−0.06(3.6)	0.34(32)	0.24(7.2)	0.06(0.9)	0.30(29)	0.39(50)	0.29(8.3)
100	−0.05(0.9)	0.25(5.1)	0.30(7.1)	0.07(0.4)	0.57(12)	0.40(8.6)	0.40(8.9)
200	0.15(1.1)	0.31(2.3)	0.41(7.5)	−0.07(0.2)	−0.60(4.4)	0.54(4.1)	0.62(11)
500	−2.91(6.8)	0.56(1.4)	0.66(8.8)	−0.41(0.4)	1.23(3.0)	1.19(2.9)	0.94(12)
1000	12.09(13)	0.74(0.8)	0.83(8.7)	−0.92(0.5)	−1.88(2.1)	0.60(0.7)	1.22(12)
2000	−18.31(9.7)	0.95(0.5)	0.93(7.7)	−3.09(0.8)	−30.10(16)	−2.53(1.4)	1.30(10)
MAE	2.60(4.3)	0.31(8.4)	0.31(7.5)	0.38(5.6)	2.70(8.0)	0.53(12)	0.43(9.1)

[a] Reference values used to deduce basis set errors are from Ref. 4. For the $1s^22s^2$ state of Be atom, reference values are from our own calculation by using very large basis sets including multiple sequences.[23] See text for details.

TABLE VI. Basis set errors for the B singly positive ion and B atom in **B** fields.[a] (Absolute errors are in mH, numbers in parentheses are the relative errors in millionths, and **B** is in a.u.)

	B^+				B					
B (a.u.)	$1s^22s^2$	$1s^2$ $2s2p_{-1}$	$1s^2$ $2p_{-1}3d_{-2}$	$1s2p_{-1}$ $3d_{-2}4f_{-3}$	$1s^22s^2$ $2p_{-1}$	$1s^22s$ $2p_02p_{-1}$	$1s^22s$ $2p_{-1}3d_{-2}$	$1s^22p_0$ $2p_{-1}3d_{-2}$	$1s^22p_{-1}$ $3d_{-2}4f_{-3}$	$1s^22p_{-1}$ $3d_{-2}4f_{-3}5f_{-4}$
0.0	0.00(0.0)	0.15(6.4)	0.06(2.8)	0.10(6.7)	0.11(4.5)	0.10(4.0)	0.18(7.4)	0.07(2.7)	0.14(6.0)	0.14(9.1)
0.1	−0.00(0.0)	0.25(10)	0.17(7.2)	0.29(19)	0.20(8.3)	0.17(7.1)	0.43(18)	0.23(9.4)	0.38(16)	0.21(13)
0.2	−0.00(0.2)	0.37(15)	0.23(9.6)	0.20(12)	0.49(20)	0.33(13)	0.40(16)	0.20(8.1)	0.23(9.6)	0.19(12)
0.5	0.01(0.4)	0.11(4.6)	0.10(4.2)	0.17(10)	0.17(7.0)	0.22(8.9)	0.13(5.2)	0.19(7.5)	0.15(6.2)	0.14(8.1)
1	0.04(1.8)	0.05(2.1)	0.15(6.1)	0.14(7.8)	0.12(5.0)	0.18(7.1)	0.08(3.3)	0.22(8.8)	0.17(6.8)	0.13(7.0)
2	0.10(4.4)	0.07(2.7)	0.19(7.3)	0.13(6.6)	0.25(10)	0.18(6.8)	0.10(3.7)	0.23(8.8)	0.21(7.9)	0.14(7.1)
5	0.19(10)	0.13(5.1)	0.34(13)	0.15(6.1)	0.23(11)	0.24(9.1)	0.16(5.8)	0.26(9.4)	0.35(13)	0.29(12)
10	0.11(8.7)	0.13(4.9)	0.41(15)	0.18(6.1)	0.21(13)	0.21(7.9)	0.28(10)	0.22(8.0)	0.47(17)	0.21(7.2)
20	0.10(47)	0.19(8.5)	0.56(22)	0.20(5.5)	0.37(135)	0.21(8.8)	0.33(13)	0.33(13)	0.68(26)	0.29(7.8)
50	0.20(4.0)	0.51(77)	0.86(81)	0.46(9.3)	0.89(21)	0.33(41)	0.76(69)	0.74(66)	0.97(74)	0.61(12)
100	0.08(0.5)	0.42(15)	0.67(29)	0.58(9.1)	0.88(6.9)	2.15(79)	1.19(53)	0.72(32)	0.82(42)	0.80(12)
200	0.03(0.1)	0.02(0.2)	0.67(6.6)	0.77(9.3)	0.78(2.5)	−2.84(26)	−0.58(5.8)	0.48(4.8)	0.93(9.6)	1.11(13)
500	−0.06(0.1)	−0.27(0.7)	1.12(3.1)	1.18(10)	0.84(1.0)	27.7(74)	23.4(64)	0.62(1.7)	1.50(4.2)	1.59(13)
1000	−0.11(0.1)	5.78(6.9)	1.47(1.8)	1.45(9.8)	−0.36(0.2)	−63.1(75)	−63.6(77)	2.48(3.0)	2.10(2.6)	2.04(13)
2000	−0.52(0.1)	−25.9(14)	1.99(1.1)	1.69(9.0)	0.36(0.1)	0.34(0.2)	0.94(0.5)	−13.3(7.5)	2.82(1.6)	2.80(14)
MAE	0.10(5.2)	2.29(12)	0.60(14)	0.51(9.1)	0.42(16)	6.55(25)	6.17(23)	1.35(13)	0.80(16)	0.71(11)

[a] Reference values used to deduce basis set errors are from Ref. 4. For the $1s^22s^2$ state of the B^+ ion and the $1s^22s^22p_{-1}$ state of the B atom, reference values are from our own calculation by using very large basis sets including multiple sequences.[23] See text for details.

TABLE VII. Basis set errors for the C atom in **B** fields.[a] (Absolute errors are in mH, numbers in parentheses are the relative errors in millionths, and **B** is in a.u.)

B (a.u.)	$1s^22s^2$ $2p_02p_{-1}$	$1s^22s$ $2p_02p_{-1}2p_1$	$1s^22s$ $2p_02p_{-1}3d_{-2}$	$1s^22p_02p_{-1}$ $3d_{-2}4f_{-3}$	$1s^22p_{-1}3d_{-2}$ $4f_{-3}5f_{-4}$	$1s^22p_02p_{-1}$ $4f_{-3}5f_{-4}$	$1s2p_{-1}3d_{-2}$ $4f_{-3}5g_{-4}6h_{-5}$
0	0.35(9.4)	0.04(1.2)	0.35(9.5)	0.18(5.0)	0.22(6.1)	0.21(8.7)	0.33(14)
0.1	0.50(13)	0.18(4.8)	0.55(15)	0.38(10)	0.34(9.5)	0.20(8.0)	0.48(20)
0.2	0.77(20)	0.06(1.6)	0.81(21)	0.16(4.5)	0.31(8.5)	0.18(7.2)	0.41(17)
0.5	0.56(15)	0.32(8.4)	0.66(17)	0.32(8.5)	0.32(8.7)	0.37(14)	0.38(15)
1	0.41(11)	0.38(9.8)	0.38(9.6)	0.32(8.4)	0.30(8.0)	0.42(15)	0.37(14)
2	0.54(14)	0.40(10)	0.38(9.4)	0.26(6.5)	0.40(10)	0.49(16)	0.38(13)
5	0.89(25)	0.46(12)	0.64(15)	0.39(9.3)	0.45(11)	1.36(38)	0.62(18)
10	0.56(18)	0.56(16)	0.43(9.9)	0.24(5.5)	0.73(16)	0.52(12)	0.60(14)
20	0.28(14)	0.18(7.1)	0.43(9.9)	0.46(10)	1.08(24)	0.60(12)	0.61(12)
50	1.12(52)	0.68(48)	1.02(31)	0.95(26)	1.27(34)	1.07(15)	1.39(19)
100	1.27(12)	0.96(10)	0.95(199)	0.70(79)	1.63(143)	1.22(14)	1.51(16)
200	1.29(4.6)	1.27(4.9)	1.25(19)	5.71(94)	1.73(30)	3.68(32)	2.08(17)
500	2.22(2.7)	2.15(2.7)	1.84(5.8)	3.25(11)	2.37(7.9)	3.53(22)	3.11(18)
1000	2.23(1.2)	2.12(1.2)	1.77(2.3)	0.72(1.0)	3.15(4.2)	−3.52(17)	3.29(15)
2000	1.14(0.3)	1.85(0.5)	1.54(0.9)	0.90(0.5)	4.89(2.9)	…[b]	4.32(16)
MAE	0.94(14)	0.78(9.3)	0.87(25)	1.00(19)	1.28(22)	1.24(16)	1.33(16)

[a] Reference values used to deduce basis set errors are from Ref. 4.

[b] Convergence was not reached.

MAEs for each atom also vary considerably, but the relative errors for each atom are always a few to 25 parts in a million, again suggesting that our new basis set construction provides relatively uniform accuracy for different atoms.

We did not find enough benchmarked energies in the literature for atoms with $Z \geq 7$ in an arbitrary B field to provide a meaningful test, hence those atoms are not included in this study, nor did we test our newly constructed basis sets for molecules because our current code can only do single-center systems, i.e., atoms.

IV. SUMMARY AND CONCLUSIONS

AGTO basis functions are well adapted to the treatment of atoms and molecules in arbitrarily strong magnetic fields.[15] But the complexity and high cardinality of existing AGTO sets has impeded their use in such calculations. This criticism is valid for our earlier scheme,[23] even though it provided the substantial advantage of a fixed, prescribed basis set rather than case-by-case optimization. The present work represents a significant technical advance based upon detailed physical analysis and extensive numerical exploration. The combination enables establishment of a few key principles to guide basis set construction. Those principles are as follows: (1) The more diffuse the function (smaller exponents), the larger the asphericity (relative difference between the transverse and longitudinal exponents of the basis function), with the limit of $B/4$ for the most diffuse functions, which is actually a Landau orbital; (2) more densely spaced functions are put in the range of exponents across which asphericities change most rapidly; (3) when more than one atomic shell is occupied by electrons for a single kind of orbital, a second sequence of basis functions is required, but the second sequence can be limited to the range over which asphericities change rapidly, e.g., $[0.03B, 0.225B]$; (4) the interaction of a 1s electron with other electrons, or the interaction between two electrons when the 1s orbital is doubly occupied, can slightly reduce the asphericity of the tight basis functions in the basis set.

With these guidelines, we first investigated, in detail, the hydrogen iso-electronic sequence in an arbitrary B field. Exploration of the transverse exponent parameter space $\{\alpha_j\}$ with full numerical optimization leads to fitting the results with a newly designed expression which takes into account the orbital quantum numbers. By fine tuning the constants in the expression, we obtained Eqs. (10)–(15). The residual basis error from this newly constructed AGTO basis sets is no more than a few μhartrees, while the relative error is only a few millionths.

For light multiple-electron atoms and ions, we further considered the strong electron-electron repulsion at the vicinity of nucleus, the aforementioned point (4), and slightly modified the basis sets of single-electron systems, leading to Eqs. (16) and (17), which depend on orbital quantum numbers and electron occupation numbers, as well as on the B field strength and nuclear charge Z. If more than one shell of a kind of orbital is occupied, we find it necessary to supplement the main sequence with a second basis function sequence in the exponent range of rapidly changing asphericity of primitives, Eqs. (18). While absolute basis set errors vary noticeably, from a few hundredths to a few of mH, the relative errors are similar for different atoms and ions in a wide range of B field strengths, indicating that our currently constructed basis sets have satisfactorily near-uniform accuracy.

We have not studied contraction of the newly constructed basis primitives but believe it could be done without any significant difficulty. Contracting primitives can reduce the number of basis functions, a desirable step for correlated wavefunction calculations and one which can be helpful in DFT calculations. Without contraction, the residual basis set errors in the newly constructed basis sets are two to three orders of magnitude smaller than the electron correlation energies in the atomic and ionic systems investigated here. Hence our basis sets should be sufficiently accurate for correlated wavefunction or DFT calculations.

SUPPLEMENTARY MATERIAL

See supplementary material for (under GPL) our computer code (written in C) which generated all the AGTO basis sets used in this work. A few examples are also included. They are also available to download from www.qtp.ufl.edu/ofdft.

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