Atomic basis functions for molecular electronic structure calculations

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Electronic structure methods for accurate calculation of molecular properties have a high cost that grows steeply with the problem size, therefore, it is helpful to have the underlying atomic basis functions that are less in number but of higher quality. Following our earlier work [Chem. Phys. Lett. 416, 116 (2005)] where general correlation-consistent basis sets are defined, for any atom, as solutions of purely atomic functional minimization problems, and which are shown to work well for chemical bonding in molecules, we take a further step here and define a new kind of atomic polarization functionals, the minimization of which yields additional sets of diffuse functions that help to calculate better molecular electron affinities, polarizabilities, and intermolecular dispersion interactions. Analytical representations by generally-contracted Gaussian functions of up to microhartree numerical accuracy grades are developed for atoms Hydrogen through Nobelium within the four-component Dirac-Coulomb theory and its scalar-relativistic approximation, and also for Hydrogen through Krypton in the two-component nonrelativistic case. The convergence of correlation energy with the basis set size is studied, and complete-basis-set extrapolation formulas are developed.

I. INTRODUCTION

The idea that the molecular electronic structure problem can be solved in terms of atom-centered basis functions is as old as the quantum theory of electron itself, but its computational realization has gone a long way from qualitative pictures to accurate quantitative predictions of molecular properties and reactivity. Atomic functions of exponential type were the first to be used for molecular calculations at the Hartree-Fock (HF) and limited configuration interaction (CI) level; within the density-functional theory, they are still widely used thanks to the numerical integration of higher angular momentum, and it was around that time that the need for a more general construction was important, as were multiple polarization functions, also found to be

Later, the so-called diffuse functions were the first to be used for molecular calculations at the Hartree-Fock (HF) and limited configuration interaction (CI) level; within the density-functional theory, they are still widely used thanks to the numerical integration and density-fitting schemes speeding up the calculations, and are optimized for all atoms within the zeroth-order regular approximation. Gaussian-type functions are unique among all classes of elementary functions in that all multicenter molecular integrals can be computed analytically, and they have become the standard primitive basis in correlated molecular calculations. Other kinds of functions can be least-squares fitted by sums of primitive Gaussians, this was done first for the exponentials and was popular for some time, but it soon became clear that energy-optimized Gaussian approximations of atomic HF wavefunctions work much better and are a must-have part of a good basis set. The low variational flexibility of the minimal basis was understood, so radial and angular polarization functions began to be added, often tweaked by hand to get better computed properties of a favorite set of small molecules. Later, the so-called diffuse functions were found to be important, as were multiple polarization functions, also of higher angular momentum, and it was around that time that the need for a more general construction was felt.

The many-body perturbation theory at second order (MP2), third, fourth, and seldom fifth order, as well as the coupled-cluster with single and double (CCSD) and perturbative triple (CCSD(T)) substitutions are a family of systematic methods approaching chemical accuracy in the complete basis limit, their fifth- to seventh-power scaling with the system size soon makes the integral evaluation, with its fourth-power scaling, a small part of the work, so one can be generous in the choice of the primitive expansion length. Moreover, there are cubic-scaling integral evaluation techniques with down to quadratic scaling with the primitive set size: the pseudospectral decomposition can even reduce the scaling of the correlation energy calculation; the density-fitting (resolution-of-identity) approximation speeds up the MP2 calculations, greatly lowers the memory usage, and is highly parallelizable.

Atomic natural orbitals (ANO) were introduced for the general contraction of Gaussian basis sets, and this is indeed a general method as, ideally, only the well-defined atomic solutions would be enough; for the Hydrogen atom, however, one had to use the H₂ molecule, and the same would have to be done for all atoms with one valence electron. No general way to add the diffuse functions within the ANO method seems to be found, the authors resorted to uncontracting or adding primitive Gaussians whose exponents may be quite arbitrary. Unfortunately, the natural occupation numbers have no direct connection to the correlation energy contribution.

The overwhelming breakthrough in the field is the development of the now-classic correlation-consistent basis set — systematic sequences of energy-optimized sets of single-Gaussian polarization functions added to generally-contracted minimal HF sets, with an option for core-core and core-valence correlation; the convergence with growing set size allows the extrapolation to the (apparent) complete basis set limit; single-Gaussian diffuse functions optimized on atomic an-

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ions can also be added — even though some atoms have a too small or no electron affinity, the limited single-Gaussian functional form helps to get meaningful exponents for typical molecular applications, more diffuse even-tempered sets are used for electrical response properties. It is remarkable, how well the single-Gaussian form works for the lighter atoms (up to Ne), although slightly less so already for the second row. But it is also clear, that a somewhat greater accuracy can be achieved with the same number of functions if they are made up from longer primitive sets.

New approaches are evolving: a completeness profile can be used to set up a black-box minimization procedure that yields completeness-optimized basis sets; bound virtual states of multiply-ionized atoms are used as polarization functions in the numerical grid-based atomic basis sets for density-functional calculations; polarization-consistent basis sets are optimized, on a set of prototypical molecules, for faster convergence of HF energy, and also for density-functional calculations; aiming at specific intermolecular potentials, interaction-optimized basis sets can be constructed by direct minimization of the counterpoise-corrected interaction energy for the dimer.

We have also found a new way to define atomic basis functions as solutions of atomic variational problems — the closed-shell MP2 correlation energy expression is used as a general minimization functional to drive the optimization of virtual space. It is generalized to be applied to all atoms (even Hydrogen) by the use of an effective Hamiltonian constructed from the spherical average-of-configurations Fock operator, which can be understood as a model of an atom in a closed-shell-like molecular environment. The use of the simplest MP2 functional seems to be no serious limitation as can be seen from the comparison with the classic basis sets of the same size in molecular CCSD benchmarks. (The molecular MP2-optimized virtual space was shown in tests to be close to optimal also for the high-level correlated methods such as CCSD.) Our method fits naturally to the four-component wavefunction theories, such as Dirac-Coulomb Hamiltonian and its scalar-relativistic approximation, and yields the atomically-balanced contraction of kinctically-balanced primitive sets. All chemically-interesting atoms have been covered and the sets have been used and worked well in the studies of compounds with atoms as heavy as actinides. Still, the limitations show up when one tries to study intermolecular potentials, dipole polarizabilities, and negatively-charged molecular systems — the functions optimized for the correlation energy of the neutral atom are too localized, and diffuse functions are missing in the set. We sought a general solution to this problem. Lowest Rydberg states were tried in this role, but are too diffuse for a typical use. From the known connection between the ionization potential and the long-range behavior of the density follows that a minimal set of diffuse functions (one for each angular symmetry) cannot fit for all imaginable atomic (or even neutral) species, and a lower bound for the ionization potential should be set anyway.

After years of thinking, we found new closed-shell-like polarizability functionals, derived from a simplified (double) perturbative treatment of atomic electron affinity at the MP2 level, whose minimization yields a first set of diffuse atomic basis functions that already recover most of the dipole polarizability and C₆ dispersion coefficient and help to get accurate intermolecular potentials for neutral molecules, and are also helpful for anionic species with strong enough electron binding. We find a way to get further diffuse function sets to be used for molecules with as low ionization potential as needed. All these variational procedures can be used to contract the primitive sets of Gaussian (or other well-behaved) functions, and we have also worked out a weighted least-squares fitting technique to optimize the primitive sets of any size needed to get a given accuracy. Here we present these new ideas (after a short review of our older underlying work) and show how they are used to make a database of atomic basis sets for all atoms from Hydrogen through Nobelium. We also study the convergence and extrapolation towards the complete basis limit on a few atoms and molecules.

II. THEORY

Our general atomic basis functions can be either four-component spinors of the Dirac-Coulomb theory (or its scalar-relativistic approximation), or the non-relativistic two-component wavefunctions. They can be defined either as solutions of integro-differential equations or as linear combinations of some primitive functions whose coefficients are solutions of constrained functional optimization problems, the latter algebraic formulation is more practical and will be given here.

We begin with a set of N₀ occupied wavefunctions \{ϕᵢ\} that make the average-of-configurations Hartree-Fock energy

\[ E₀ = \sum_{i=1}^{N₀} wᵢHᵢᵢ + \frac{1}{2} \sum_{i,j=1}^{N₀} aᵢⱼwᵢRᵢᵢ,jⱼwⱼ \]  \hspace{1cm} (1)

stationary (the orthogonality constraints are always implied). The one-electron \{Hᵢᵢ\} and antisymmetrized two-electron \{Rᵢⱼ\} integrals are computed over the given set of N two-component (or 2N four-component) primitive functions \{ϕᵢ\} and transformed with coefficients Cᵢⱼ to those in Eq. (1). The occupancies 0 < wᵢ ≤ 1 and the coupling coefficients aᵢⱼ = aⱼᵢ are such as keep the spherical symmetry of a neutral atom, in the closed-shell case wᵢ = 1, aᵢⱼ = 1. The stationarity conditions are

\[ Hᵢᵢ + \sum_{j=1}^{N₀} aᵢⱼRᵢᵢ,jⱼwⱼ = 0 \]  \hspace{1cm} (2)
where \( u > N_0 \) counts all unoccupied states, and also
\[
(w_i - w_j)H_{ij} + \sum_{k=1}^{N_0} (a_{ik}w_i - a_{jk}w_j) R_{ij,kk}w_k = 0. \tag{3}
\]
The occupied energies
\[
\epsilon_i = F_{ii}^o \tag{4}
\]
are set to the diagonal elements of the Fock matrix
\[
F_{ij}^o = H_{ij} + \frac{1}{2} \sum_{k=1}^{N_0} (a_{ik} + a_{jk}) R_{ij,kk}w_k, \tag{5}
\]
and if the energy of Eq. (1) is invariant to rotations for some \( i,j \)-pair, then the condition
\[
F_{ij}^o = 0 \quad \text{for} \quad i \neq j, \quad w_i = w_j, \quad a_{ik}w_i = a_{jk}w_j, \tag{6}
\]
should also be met. For the virtual subspace, the Fock matrix is taken to be
\[
F_{\mu\nu}^v = H_{\mu\nu} + \sum_{i=1}^{N_0} R_{\mu\nu,ii}w_i, \tag{7}
\]
in the four-component case, it is diagonalized in that subspace to get \( N - N_0 \) electronic and \( N \) positronic states, the latter being discarded and all further work is done within the electronic part.

For some atoms, there are low-lying states not included in the average of Eq. (1) but important for chemical bonding, so \( N_1 \) functions should be added to the occupied set \( \{ \phi_i \} \) to account for it, and this is done by the diagonalization of a Fock matrix
\[
F_{\mu\nu}^v = H_{\mu\nu} + \sum_{i=1}^{N_0} R_{\mu\nu,ii}w_i, \tag{8}
\]
in the space of \( N - N_0 \) virtual electronic wavefunctions,
\[
F_{ij}^v = \epsilon_i \delta_{ij} \quad \text{for} \quad i,j > N_0, \tag{9}
\]
\( N_1 \) such states with energies \( \epsilon_i \) go into the occupied set that from now on has the size \( N_o = N_0 + N_1 \). The occupancies \( w_i^o \) are for the spherically-averaged configuration of the singly-ionized atom.

At this time, we build the effective Fock operator
\[
\hat{F} = \sum_{i=1}^{N_o} |\phi_i\rangle \langle \phi_i| + \sum_{i,j=1}^{N_0} (1 - |\phi_i\rangle \langle \phi_i|) \hat{F}_v (1 - |\phi_j\rangle \langle \phi_j|) \tag{10}
\]
that is spherically symmetric, and together with the two-electron interaction it is all that is needed as input to a correlation energy calculation. We forget about the fractional occupations — now we work with the (pseudo)atom as if it had the closed-shell configuration with \( N_o \) fully filled levels.

A set of \( N_v \) virtual wavefunctions \( \{ \phi_u \} \) (needed for electron correlation, atomic polarization upon chemical bonding, electron affinity, and dispersion interaction in molecules) can be grown stepwise by minimization of the functionals (shown below) defined in terms of the linearly transformed set \( \{ \phi_u \} \) with coefficients \( \{ C_{ua} \} \) that diagonalize their block of the Fock matrix
\[
\sum_{v=N_v+1}^{N_v} F_{uv}^v C_{va} = \epsilon_a C_{ua} \tag{11}
\]
and have energies \( \{ \epsilon_a \} \). The stepwise growth means that a set of \( N_v^{(1)} \) functions \( \{ \phi_u \} \) is optimized first for one functional; next, keeping these \( N_v^{(1)} \) frozen, \( N_v^{(2)} \) functions are added and optimized for another functional of all \( N_v^{(1)} + N_v^{(2)} \) functions, and so on. (Sometimes (see Section III) the very first set of \( N_v^{(0)} \) functions is taken as the next lowest energy states of Eq. (9) after the lowest \( N_v^{(1)} \).

The minimization of a model second-order correlation energy functional
\[
E_2 = \frac{1}{2} \sum_{ijab} p_{ij} |R_{ai,bj}|^2 \tag{12}
\]
with respect to some members of the set \( \{ \phi_u \} \) yields functionals nearly optimal for the most part of electron correlation in atoms and molecules. The factors \( p_{ij} \) in Eq. (12) are set to 1 or 0 to switch the valence-only, core-valence, and core-core correlation. The stationarity conditions can be derived by chain-rule differentiation with respect to rotations that mix the external \( \{ \phi_v \} \) and the virtual \( \{ \phi_u \} \) functions, and can be written as
\[
G_{xu} = \sum_a \left( G_{xa} + \sum_b F_{xb} D_{ab} \right) C_{ua} = 0 \tag{13}
\]
with
\[
G_{xa} = \sum_{ijb} p_{ij} R_{ai,bj} R_{ai,bj}. \tag{14}
\]
\[
D_{ab} = \sum_{ijc} (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_c). \tag{15}
\]
The second derivatives of Eq. (12) can also be derived and used in an efficient quadratically-convergent Newton-Raphson optimization with a careful steps size control.

Until now, we have followed our earlier work\(^{24}\), but since then the experience has shown that such atomic basis sets lack diffuse functions needed for accurate calculation of electron affinities, polarizabilities, and dispersion interactions in molecules. Now, we have found a model polarization functional
\[
E_a = \sum_{ia} p_i |\hat{U}_{ai}|^2, \tag{16}
\]
whose minimization yields a set of functions, with angular momenta up to those in the occupied set, that help to account for the changes upon electron attachment (or detachment). The occupancies \( \tilde{w}_i \) add up to one and are spherically-averaged, typically \( \tilde{w}_i = \bar{w}_i - w_i^+ \), the switching factors \( p_i \) are set to 1 or 0. Eq. (16) can be understood as the second-order perturbative correction for the averaged electron attachment energy at the Hartree-Fock level, and we believe it to be a better functional for driving the diffuse function optimization than the directly computed energy of an atomic anion — some atoms have a tiny or no electron affinity so the functions may become too diffuse, but the perturbative first order changes are more localized and still in the right direction. The stationarity conditions are as in Eq. (13) but now with

\[
G_{\alpha a} = \sum_i p_i \tilde{U}_{\alpha a} \tilde{U}_{\alpha i},
\]

\[D_{ab} = \sum_{i} p_i \tilde{U}_{ai} \tilde{U}_{bi}, \]

and there is a simple explicit solution.

To optimize the diffuse functions with higher-than-occupied angular momenta, we model the changes in the MP2 correlation energy upon electron attachment. The perturbed occupied wavefunctions

\[
\tilde{\phi}_i = \phi_i + \sum_{a = N_o+1}^N \phi_a \frac{\tilde{U}_{ai}}{\epsilon_i - \epsilon_a},
\]

with the sum running here over the whole \( N - N_o \) virtual space in diagonal representation of the matrix of Eq. (7), are computed first, and then the set \( \{ \tilde{\phi}_i \} \) is used in Eq. (12) instead of \( \{ \phi_i \} \) to get the new functional \( E_2 \). The difference

\[
\Delta E_2 = \tilde{E}_2 - E_2
\]

is a measure of how the members of the set \( \{ \phi_a \} \) under optimization help to lower the correlation energy of the atomic anion more than of the neutral atom, and this is the functional that is minimized to get the set of diffuse functions. With the intermediate normalization of Eq. (20) one term in \( E_2 \) is exactly canceled by \( E_2 \), and we like it.

Here we can stop, as we now have enough tools to build systematic sequences of atomic basis set for a broad range of molecular applications. Still, we should be aware of their limitations and would like to take a look ahead towards a better sampling of the diffuse tail region. We have studied the dipole polarizability functional

\[
E_d = \sum_{ia} p_i |\mathbf{r}_{ai}|^2 \frac{\epsilon_i - \epsilon_a}{\epsilon_i - \epsilon_a},
\]

and the homoatomic \( C_6 \) dispersion coefficient functional

\[
E_6 = \frac{2}{3} \sum_{ijab} p_{ij} |\mathbf{r}_{ai}|^2 |\mathbf{r}_{bj}|^2 \frac{\epsilon_i - \epsilon_j - \epsilon_a - \epsilon_b}{\epsilon_i - \epsilon_a - \epsilon_j - \epsilon_b},
\]

where \( \mathbf{r}_{ai} \) are the dipole moment integrals, minimization of either of them yields a set of functions that are somewhat more diffuse than those based on Eqs. (16) and (21) — these can be added to the set after the former ones, but our molecular tests show this to be of little help for most molecular systems, even for noble gas dimers there is only a small lowering of the potential energy curve. Higher multipole analogs of Eqs. (22) and (23) could have been studied, but we do not feel it to be the right way forward.

A smooth sampling of the diffuse tails can be done with a one-parameter family of model Fock operators

\[
\tilde{F}_\zeta = \hat{F} + \zeta \hat{\mu},
\]

with \( \hat{\mu} \) from Eq (17) and \( 0 \leq \zeta \leq \zeta_{\text{max}} \), that can be diagonalized (with a frozen core option) to get the wavefunctions of the form

\[
\tilde{\phi}_{i\zeta} = \phi_i + \sum_{a = N_o+1}^N \phi_a \tilde{\mathcal{C}}_{ai\zeta}
\]

with energies \( \tilde{\epsilon}_{i\zeta} \), and \( \zeta_{\text{max}} \) can be found such that \( \epsilon_{N_o+\zeta_{\text{max}}} = \epsilon_{\text{max}} \). A good \( \epsilon_{\text{max}} < 0 \) can be set, for all atoms, to grow the tails as diffuse as \( \exp(-\sqrt{27\epsilon_{\text{max}}} r) \) for the new members of the set \( \{ \tilde{\phi}_u \} \), such that if the \( \tilde{F}_\zeta \) is diagonalized in the subspace to get the wavefunctions

\[
\tilde{\phi}_{i\zeta} = \phi_i + \sum_{u = N_o+1}^N \phi_u \tilde{\mathcal{C}}_{ui\zeta}
\]

with energies \( \tilde{\epsilon}_{i\zeta} \), then the integral

\[
\tilde{\epsilon} = \int_0^{\zeta_{\text{max}}} \sum_{i} \tilde{\epsilon}_{i\zeta} d\zeta
\]

is minimized. It can be seen that the functional of Eq. (16) is a lowest-order perturbative approximation to that of Eq. (27), and the functions of Eq. (20) are nothing else than first-order perturbative analogs of those of Eq. (24). In the same way, to get the higher-than-occupied functions, the integral

\[
\Delta E_2 = \int_0^{\zeta_{\text{max}}} (\tilde{E}_2(\zeta) - E_2(\zeta)) d\zeta
\]

can be minimized, where \( \tilde{E}_2(\zeta) \) is built upon the set \( \{ \tilde{\phi}_{i\zeta} \} \) instead of \( \{ \tilde{\phi}_i \} \) in \( E_2 \) of Eq. (12).

The general atomic basis functions outlined above can be computed to any meaningful accuracy by numerically
solving the underlying variational problems. Once the (nearly) exact solutions \( \{ \tilde{\phi}_k \} \) are at hand, practical approximations, such as the traditional contracted Gaussian or exponential (Slater-type) functions, can be developed for use in molecular calculations. First, we optimize the exponents of the primitive functions by weighted least-squares fitting, minimizing

\[
Q = \sum_{k=1}^{N_o+N_v} \beta_k \int \left| \tilde{\phi}_k(r) - \phi_k(r) \right|^2 w(r) \, d^3r
\]

with respect to both the linear coefficients \( \{ \tilde{c}_{nk} \} \) and the primitive exponents \( \{ \alpha_n \} \) of the approximate functions \( \{ \tilde{\phi}_k \} \), with the weights

\[
\beta_k = \begin{cases} 
\beta_0, & k \leq N_o \\
1, & k > N_o
\end{cases}
\]

made heavier for the occupied set by \( \beta_0 \), and the radial weight functions \( w(r) = 1/|r| \). After much experimentation, we set \( \beta_0 = 2^{12} \) that gives a good balance between the HF and correlation energies, and our choice of \( w(r) \) leads to the exponents that are close to the energy-optimized values in the HF case. We have tried to put the orthonormality constraints on \( \{ \tilde{\phi}_k \} \) in the fitting, but found it to heavily complicate and slow down the computations without giving better results, so we put it aside.

There is a known pitfall in the work with the exponents — some of them may be driven towards the same value whereas the linear coefficients of opposite sign go towards infinity — and this is the true but numerically unstable and impractical solution. To overcome this, we put a bound on the closeness and parametrize the exponents as

\[
\alpha_n = \exp \left( p_1 + \sum_{m=2}^{n} \sqrt{p_0^2 + p_m^2} \right),
\]

and \( \{ p_n \}, n \geq 1 \), are now taken as the optimization variables instead of \( \{ \alpha_n \} \), and thus \( \alpha_{n+1}/\alpha_n \geq \exp(p_0) \), we settle on \( p_0 = (\ln 2)/4 \) as a good compromise between accuracy and stability.

After the primitive exponents have been optimized, we run a variational calculation to get the linear coefficients, and so we get our atomic basis functions with the least-squares fitted exponents and energy-optimized linear coefficients.

III. CALCULATIONS

We have written a computer code for solving the atomic variational problems of section II with full use of spherical symmetry — the angular degrees of freedom are integrated out analytically and only the radial equations are worked with. Extended precision floating-point arithmetics with 256- or 128-bit mantissa is implemented using the X86_64 64-bit integer instruction set (with the wide multiply) in our hand-written assembly code for high speed — this overcomes the severe round-off errors arising from the near-linear dependence in a large primitive basis set of densely-spaced Gaussian functions, and the final results can be reliably rounded to the standard 64-bit precision.

We use the newest estimate\(^{88,89}\) of the speed of light \( c = 137.035999173 \) in all relativistic four-component calculations, and also the finite nucleus model\(^{88}\) with Gaussian charge distribution with exponent (in au)

\[
\alpha = \frac{3}{2} \left( \frac{529177249}{5700 + 8360 \cdot \sqrt{M}} \right)^2,
\]

where \( M \) is the (integer) mass number of the most abundant isotope; point nucleus is used in the non-relativistic case. We solve the variational problems of Section II to a very high accuracy over a huge even-tempered primitive Gaussian basis with exponents

\[
\alpha_p = 2^{p/3}
\]

where \(-69 \leq p \leq 111\), that makes 181 radial functions for each angular symmetry; we estimate the overlap between these and the exact solutions to be of the order \( 1 - 2^{-64} \) for the occupied set and somewhat less for the virtual. In the non-relativistic case, a range \(-69 \leq p \leq 225 \) would be needed to meet the nuclear cusp condition, but we find it more practical to use

\[
\alpha_p = 2^{p/3} + \exp(ap - b)
\]

with \( a \) and \( b \) optimized for each atom on its hydrogen-like ion with one electron, and a more narrow range of \( p \).

The standardized electronic configurations of atoms are shown in Table I, where \( L^+ \) is the angular momentum for which one electron is removed to get the occupancies \( w_i^{(0)} \) in Eq. (8), \( L_1 \) is for the \( N_i \) functions of Eq. (9) added to the occupied set, \( L_2 \) is for the first \( N_i^{(0)} \) virtual functions also from Eq. (9), and the atoms are marked for which the diffuse functions may be added. To get the coupling coefficients in Eq. (11), we use the average level\(^{11}\) formalism in the Dirac-Coulomb case, and also the usual average of the highest-spin configurations in the scalar-relativistic and non-relativistic cases.

The stepwise optimization begins with the outermost occupied shell block (of the same principal quantum number \( n \)), for which the functional of Eq. (12) with valence-only \( p_{ij} \) is minimized first to get a set of virtual functions \( N_{in}^{v} \) radial parts for each angular momentum \( l \), then a set of diffuse functions may be optimized using Eq. (16) followed by Eq. (21); the next block of inner valence (for transition metals) or core shells may then be taken and the virtuals optimized using Eq. (12) with \( p_{ij} \) set to core-core and core-valence correlation, and so on to the innermost core shells. The correlation-consistent virtual set sizes at each step are taken to be

\[
N_{in}^{v} = \max(\lambda_n - \max(l - l_n^{\max} - 1, 0), 0)
\]
where $l_{\text{max}}^\text{n}$ is the highest occupied angular momentum of the $n$-block, and $\lambda_n$ is the set number (1, 2, 3, 4) for this $n$ — thus $l$ reaches up to $l_{\text{max}}^\text{n} + \lambda_n$ and there are $\lambda_n$ radial parts for $l \leq l_{\text{max}}^\text{n} + 1$. The size of the diffuse set is simply $N_{\text{diff}} = 1$ for $l \leq l_{\text{max}}^\text{n} + \lambda_n$. The same $\lambda_n$ is typically used for all $n$, but our code can work with any other settings.

For most metal atoms, the outermost core shells should be unfrozen. Table II shows the number of the $n$-blocks that are always correlated. One may also note the atoms Ca, Sr, Ba, and Ra to have a shell added ($L_2$) to the unoccupied set, we found it to be the key to get the accurate bonding properties of these “subtransition” metals, to cure the known pathology.

### TABLE I. Atomic electronic configurations.

| atoms     | number of electrons | $L^+$ | $L_1$ | $L_2$ | diffuse | $n^9$ |
|-----------|---------------------|-------|-------|-------|---------|-------|
| H, He     | 1+                  | 0     | +     |       | 1       |       |
| Li, Be    | 3+                  | 0     | 1     |       | 2       |       |
| B – Ne    | 4, 1+               | 1     | +     |       | 1       |       |
| Na, Mg    | 5+, 6               | 0     | 1     |       | +       | 1     |
| Al – Ar   | 6, 7+               | 1     | +     |       | 1       |       |
| K         | 7, 12               | 0     |       |       | 2       |       |
| Ca        | 8, 12               | 0     | 1     | 2     |       |       |
| Sc – Zn   | 8, 12, 1+           | 0     | 1     | 2     |       |       |
| Ga – Kr   | 8, 13+, 10          | 1     | +     |       | 1       |       |
| Rb        | 9, 18, 10           | 0     | 1     |       | 2       |       |
| Sr        | 10, 18, 10          | 0     | 1     | 2     |       |       |
| Y – Cd    | 10, 18, 11+         | 0     | 1     | 2     |       |       |
| In – Xe   | 10, 19+, 20         | 1     | +     |       | 1       |       |
| Cs        | 11, 24, 20          | 0     | 1     | 2     |       |       |
| Ba        | 12, 24, 20          | 0     | 1     | 2     |       |       |
| La        | 12, 24, 21          | 0     | 1     | 2     |       |       |
| Ce – Yb   | 12, 24, 21, 1+      | 0     | 1     |       | 3       |       |
| Lu – Hg   | 12, 24, 21+, 14     | 0     | 1     |       | 2       |       |
| Ti – Rn   | 12, 25+, 30 , 14    | 1     |       |       | 2       |       |
| Fr        | 13, 30, 30, 14      | 0     | 1     | 2     |       |       |
| Ra        | 14, 30, 30, 14      | 0     | 1     | 2     |       |       |
| Ac        | 14, 30, 31, 14      | 0     | 1     | 2     |       |       |
| Th – No   | 14, 30, 31, 15+     | 0     | 1     | 2     |       |       |
|           |                     |       |       |       |         |       |

$^9$ Number of electrons for each angular momentum; the plus + means the number grows in the row starting with the given value.
$^b$ Whether the diffuse functions are added.
$^c$ At least $n$ of the outermost principal quantum number shell blocks are correlated.

With the nearly-exact solutions at hand, the least-squares optimization based on Eq. (29) is run to get the primitive basis sets of growing size — this can be done either separately and independently for each angular momentum $l$, or all at once with the exponents shared between all $l$. The former is more flexible, economical, and natural, so we do most of our work this way; but the latter is helpful to speed up some electronic structure methods if the integral evaluation can make use of shared exponents, so we also do it on a smaller scale. The non-linearization of exponents sometimes finds multiple minima, and we often had to feed it with several sets of starting values, made by hand, to get either the lowest error or, more seldom, a more regular variation of the exponents with the atomic number. We have always seen the close-to-exponential convergence of the fit error with the primitive set size $M_l$, and the same is also true for both the HF- and MP2-energy errors, which we estimate for a given $M_l$ by running atomic calculations on the sets of size $\{\tilde{M}_0, \ldots, \tilde{M}_{l-1}, M_l, \tilde{M}_{l+1}, \ldots, \tilde{M}_{\text{max}}\}$ and $\{M_0, \ldots, M_{\text{max}}\}$ and subtracting the energies, where $\tilde{M}_l$ are big enough. Thus we grade the primitive sets by their energy errors $E_l(M)$ for each $l$, and now we have to decide on the standard set sizes $\{M_l^{(\kappa)}\}$ so that $E_l(M_l^{(\kappa)}) \approx E^{(\kappa)}$ for all $l$ and for both HF and MP2, that is, the errors are of the same order, and for $\kappa = 1, 2, \ldots$ we should have the errors close to a geometric series $E^{(\kappa)}/E^{(\kappa-1)} \approx \varepsilon$. As a guide, we look at the MP2 values of $E_{\text{max}}^{(\kappa)}$ for $\kappa = 1, 2, \ldots, 5$ for atoms He and Ne, and we see $\varepsilon \approx \frac{1}{3}$, and so we align all our sets for all atoms.

For $\lambda_n = 1, 2, 3, 4$ and $5$ for lighter atoms in Eq. (35) and $\kappa = 1, 2, 3, 4, 5$, with and without the correlation of the outermost or all core electrons, we have optimized the series of basis sets for atoms H through No (7682 in number) for both the Dirac-Coulomb Hamiltonian and its scalar-relativistic approximation, and also for H through Kr for the non-relativistic case. It took us years of hard work at which we grew old and sick, so we cannot give all details here. Instead, the files in the supplementary material hold all our data sets (to 64-bit precision) and everyone is welcome to use them or to study their properties.

Our mnemonics for the optimized atomic basis sets are:

- $LL\lambda\kappa$ for the valence-only correlation,
- $LL\lambda\kappa$ the same with the diffuse functions,
- $LL\lambda\kappa$, $LL\lambda\lambda\kappa$ with the outermost core shells included into the correlation,
- $LL\lambda\kappa$, $LL\lambda\lambda\kappa$ the same with the diffuse functions,
- $LX\lambda\kappa$ for all-electron correlation,
- $LX\lambda\kappa$ the same with the diffuse functions.

It would have been good to test all these on a set of molecules, but here we will only study the convergence and extrapolation towards the complete basis limit on a few simple but characteristic examples.

### TABLE II. MP2 correlation energy of closed-shell atoms.

| $\lambda$ | $LL\lambda$ | $LX\lambda$ |
|-----------|-------------|-------------|
| He        | -0.2285774  | -0.3038974  |
| Ne        | -0.3418358  | -0.3473452  |
| Li         | -0.03585425 | -0.03610341 |
| B          | -0.03653868 | -0.03667322 |
| Mg         | -0.03608650 | -0.03694147 |
| Al         | -0.03704621 | -0.03709066 |
| Si         | -0.03715014 | -0.03717877 |
| P          | -0.03721486 | -0.03723414 |
| S          | -0.03745721 | -0.03727069 |
| Cl         | -0.0373774  | -0.302621    |
| Ar         | -0.191321   | -1.2032      |

The atoms He, Ne, and Ni in Table II are archetypal for the closed-shell correlation, and we took pains to go up to $\lambda = 9$ to come close to the asymptotic behavior.
(For Ni, the sets are not for the standard configuration of Table I but for the closed-shell state with 18 outer electrons correlated.)

A natural functional form

$$E_\lambda \approx E_\infty + \sum_{p=3}^{P} \frac{A_p}{(\lambda + p)^p}$$  \hspace{1cm} (36)

with some small $P > 3$ can be used to fit the computed $E_\lambda$ for a range of $\lambda$ and thus to get an estimate of $E_\infty$. The only nonlinear parameter $\nu$ in Eq. (36) can be adjusted each time, but we find $\nu = \frac{3}{2}$ to be a good fixed value, often very close to the optimal one, and we set it so everywhere in the following. By fitting through $P - 1$ points $\lambda = \lambda_0, \ldots, \lambda_0 + P - 2$, each time for a higher $\lambda_0$, we can also estimate the residual error of the last $E_\infty(\lambda_0)$ as $E_\infty(\lambda_0) - E_\infty(\lambda_0 - 1)$, this way we get the limits $E_\infty$ in Table II seemingly converged to all digits given. With these at hand, we can try to find a simple and practical two-point extrapolation formula of the kind

$$E_\infty \approx E_\lambda + (E_\lambda - E_{\lambda-1})c_\lambda$$  \hspace{1cm} (37)

that would follow if it would hold that

$$E_\lambda \approx E_\infty + Ab_\lambda,$$  \hspace{1cm} (38)

with the universal $b_\lambda$, so that

$$c_\lambda = b_\lambda/(b_{\lambda-1} - b_\lambda).$$  \hspace{1cm} (39)

Computing

$$\tilde{c}_\lambda = (E_\infty - E_\lambda)/(E_\lambda - E_{\lambda-1}) \approx c_\lambda$$  \hspace{1cm} (40)

over the data set of Table II we see that $\tilde{c}_\lambda$ are weakly system dependent, and a conservative approximation to Eq. (39) is simply the shortest form of Eq. (36).

$$E_\lambda \approx E_\infty + A/(\lambda + \frac{3}{2})^3,$$  \hspace{1cm} (41)

and thus

$$c_\lambda = 1/\left(1 + 1/(\lambda + \frac{1}{2})^3 - 1\right).$$  \hspace{1cm} (42)

We have tried to find better extrapolation formulas by splitting the two-electron correlation energy into its spin components — the same-spin part is known to have $A_3 = 0$ in Eq. (30) — but could not get a higher overall accuracy. The CCSD correlation energy can as well be extrapolated in the same way — we have found it to be of no help to split it into the MP2 and higher-order parts, as the latter does not seem to show a regular behavior, at least for smaller $\lambda$. The perturbative triples energy of CCSD(T), however, can be extrapolated well enough using the fourth power instead of the third in Eqs. (41) and (42).

Molecular tests in Tables III and IV show the convergence with respect to both the number of basis functions and the quality of their approximation with the underlying primitive set size. The three molecules, H$_2$, N$_2$, and LiF, are prototypical for covalent and ionic bonding and, because of the very regular and consistent structure of our basis sets across the periodic table, Table III can guide the choice of the right set for a given application. At the other end, the weakest bonding in the noble gas dimers He$_2$ and Ne$_2$ studied in Table IV should be under-

| Table III. MP2 calculations on H$_2$, N$_2$ and LiF molecules. |
|------------------|------------------|------------------|------------------|
| H$_2$  | r | $\Delta E$ | N$_2$  | r | $\Delta E$ | LiF  | r | $\Delta E$ |
|-------|---|-----------|-------|---|-----------|------|---|-----------|
| L$_1$ |  1.09046 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |
| L$_2$ |  1.09034 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |
| L$_3$ |  1.09034 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |
| L$_4$ |  1.09034 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |
| L$_5$ |  1.09034 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |
| L$_6$ |  1.09034 | -0.198396 |  2.10875 | -0.331133 |  3.99521 | -0.199257 |

The bond lengths $r$ and the binding energies $\Delta E$ are in au, the values in italics are extrapolated from those on the line above.
stood as the worst case performance — we see here that, without the diffuse functions, the bond lengths and energies do converge but too slowly, and our diffuse sets help to recover the most part of the attractive interaction that is somewhat overestimated and can be (over)corrected by the counterpoise method so that the two binding energies seem to bracket the "exact" value.

### TABLE IV. MP2 calculations on He$_2$ and Ne$_2$ dimers.

| set   | $r$  | $\Delta E$ | $r$  | $\Delta E$ |
|-------|------|-------------|------|------------|
| L1a   | 7.187 | -1.43       | 7.3415 | -5.59     |
| L2a   | 6.543 | -4.81       | 6.8642 | -21.93    |
| L3a   | 6.2747| -8.35       | 6.4231 | -36.40    |
| L4a   | 6.1112| -11.41      | 6.3184 | -48.17    |
| L5a   | 6.0039| -13.92      | 6.2362 | -56.85    |
| L6a   | 5.9309| -15.93      | 6.1793 | -63.69    |
| L7a   | 5.8080| -17.52      | 6.1503 | -66.30    |
| L8a   | 5.6041| -18.78      | 6.0913 | -71.42    |
| L9a   | 5.5913| -18.78      | 6.1486 | -74.94    |
| L10a  | 5.8329| -21.15      | 5.7670 | -70.77    |
| L11a  | 5.8329| -21.15      | 6.1675 | -88.86    |
| L12a  | 5.8228| -24.19      | 6.1672 | -91.99    |
| L13a  | 5.8224| -25.58      | 6.1670 | -92.50    |
| L14a  | 5.8275| -20.77      | 6.1670 | -92.50    |
| L15a  | 5.8377| -20.80      | 6.1689 | -92.50    |
| L16a  | 5.8133| -20.50      | 6.0311 | -90.36    |
| L17a  | 5.8298| -20.18      | 6.0118 | -90.21    |
| L18a  | 5.8253| -20.32      | 6.0076 | -104.79   |
| L19a  | 5.8236| -20.62      | 5.9932 | -106.00   |
| L20a  | 5.8240| -20.43      | 5.9933 | -106.22   |
| L21a  | 5.8210| -20.10      | 6.0076 | -79.39    |
| L22a  | 5.8031| -20.00      | 6.0355 | -78.59    |
| L23a  | 5.8117| -20.71      | 6.0430 | -89.68    |
| L24a  | 5.8089| -20.79      | 6.0393 | -91.77    |
| L25a  | 5.8087| -20.84      | 6.0315 | -91.89    |
| L26a  | 5.7920| -21.82      | 6.0451 | -87.45    |
| L27a  | 5.7985| -21.31      | 6.0440 | -87.46    |
| L28a  | 5.7966| -21.20      | 6.0407 | -87.71    |
| L29a  | 5.7963| -21.23      | 6.0401 | -87.84    |
| L30a  | 5.7983| -21.73      | 6.0414 | -81.62    |

The binding energies $\Delta E$ are in microhartrees and computed either relative to the isolated atoms (first column) or with the counterpoise correction (second column). The values in italics are extrapolated from those on the line above. The bond lengths $r$ are in bohrs. The extrapolation of the correlation energy at least does not hurt these weakest bonds, leading to some underbinding, but is a great improvement for the strong chemical bonds as seen in Table IV so it should be helpful for all molecular systems.

The dipole polarizabilities in Table V clearly witness the need for the diffuse functions, using Eq. (23) we add one more “b”-set in L1ab which yields the highest accuracy, but the L1a are already quite good and should be used to get the accurate intermolecular interactions.

The minimal primitive representation of angular polarization functions of our L1a, L2a, and L3a, 1 sets for lighter atoms can be compared one-to-one with that of the classical works 54, 55, 56, a remarkably close match of the exponents for atoms He, B–Ne, and Al–Ar can be seen (less so for H as we take the atom and not the H$_2$ molecule), and this must be a very good sign for us all.

### TABLE V. MP2 polarizabilities (au) of atoms and molecules.

| set   | He   | Ne   | H$_2$ | N$_2$ |
|-------|------|------|-------|-------|
| L1a   | 0.367 | 0.618 | 6.280 | 2.220 |
| L2a   | 0.675 | 1.154 | 6.430 | 3.320 |
| L3a   | 0.886 | 1.529 | 6.405 | 3.840 |
| L4a   | 1.023 | 1.802 | 6.430 | 4.114 |
| L5a   | 1.113 | 1.990 | 6.389 | 4.284 |
| L6a   | 1.203 | 2.132 | 6.577 | 4.477 |
| L7a   | 1.252 | 2.331 | 6.364 | 4.848 |
| L8a   | 1.283 | 2.445 | 6.377 | 4.500 |
| L9a   | 1.304 | 2.517 | 6.360 | 4.523 |
| L10a  | 1.318 | 2.560 | 6.351 | 4.535 |
| L11a  | 1.354 | 2.711 | 6.569 | 4.630 |
| L12a  | 1.360 | 2.712 | 6.395 | 4.547 |
| L13a  | 1.361 | 2.704 | 6.359 | 4.551 |
| L14a  | 1.360 | 2.701 | 6.351 | 4.557 |

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