

A new class of atomic basis functions for accurate electronic structure calculations of molecules

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Received 27 July 2005; in final form 6 September 2005

Available online 6 October 2005

Abstract

A new general approach is developed for obtaining systematic sequences of atomic single-particle basis sets for use in correlated electronic structure calculations of molecules. All the constituent functions are defined as the solutions of variational problems and are of three types: a minimal Hartree–Fock set, additional functions to represent low-lying excited configurations, and general functions for describing electron correlation. The latter are determined to minimize a functional derived from the closed-shell second-order correlation energy expression. Generally-contracted Gaussian expansions are developed to approximate these general functions in the non-relativistic case and within a scalar-relativistic approximation.

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1. Introduction

Electronic structure calculations of molecules are usually performed using a finite single-particle basis to expand electronic wavefunctions. For high accuracy studies of molecular properties it is essential to be able to estimate the effect of basis set incompleteness, which can be done when a systematic sequence of basis sets of increasing size is available. If atom-centered functions in the form of a product of spherical harmonics and radial functions are the most natural choice for polyatomic molecules, the question arises of the best composition of an atomic basis set, that is, the specification of the number of functions for each angular symmetry and the definition of their radial part. In this work, a new general approach is developed in which all basis functions for any atom are obtained as solutions of integro-differential equations arising from variational problems. Such functions can then be approximated to any desired accuracy by Gaussian expansions, for computational convenience. Our approach can be considered an alternative to the atomic natural orbital (ANO) method [1] as well as to the popular correlation-consistent

polarized (cc-pVXZ) basis sets [2,3]. It is designed to overcome some limitations of these approaches:

- atoms with one valence electron (in particular Hydrogen) should be treated on equal terms as any other atom, without resorting to molecular calculations for generating the basis functions;
- higher angular momentum functions should be defined in a more general form than a minimal Gaussian representation of cc-pVXZ sets, this is shown to be an important improvement [4] at least for the smaller sets;
- the functions should be (at least approximately) energy-optimized, contrary to the occupation number guided selection in the ANO method which becomes problematic [5] for treating core–valence correlation consistently;
- the method should be applicable to relativistic four-component Hamiltonians (Dirac–Coulomb in particular) whose energy spectrum is not bound from below.

2. General procedure

In our approach, a basis set for an atom is created starting from a minimal Hartree–Fock set, which is then

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augmented with functions to describe low-lying excited configurations, and finally by generating correlating functions of a new type stepwise for each occupied principal quantum number.

2.1. Minimal Hartree–Fock set

A minimal set of spatial one-particle wavefunctions $\phi_i(\mathbf{r})$ is defined to make the Hartree–Fock energy expression for an average of configurations

$$E_0 = w_i h_{ii} + \frac{1}{2} w_i [(ii|jj)a_{ij} - (ij|ji)b_{ij}] \quad (1)$$

stationary subject to orthogonality constraints

$$s_{ij} = \delta_{ij}. \quad (2)$$

Fractional occupation numbers w_i and coupling coefficients a_{ij} , b_{ij} are chosen to ensure the spherical symmetry of the effective Hamiltonian, for the closed-shell case $w_i = 2$, $a_{ij} = 2$, $b_{ij} = 1$. Here, as in the following the summation over repeated indices is implied, indices i, j, k (a, b, c) label functions from occupied (virtual) subspaces, and indices $\kappa, \lambda, \mu, \nu$ refer to any function. One-electron energies are defined as

$$\epsilon_i = f_{ii}, \quad (3)$$

$$f_{ij} = h_{ij} + (ij|kk)a_{jk} - (ik|kj)b_{jk}, \quad (4)$$

the closed-shell blocks of the Fock matrix are chosen diagonal,

$$f_{ij} = \epsilon_i \delta_{ij}, \quad \text{if } w_i = w_j = 2. \quad (5)$$

In the non-relativistic case the one- and two-electron integrals are defined as

$$s_{\kappa\lambda} = \int \phi_\kappa(\mathbf{r}) \phi_\lambda(\mathbf{r}) d^3\mathbf{r}, \quad (6)$$

$$h_{\kappa\lambda} = \frac{1}{2} \int \nabla \phi_\kappa(\mathbf{r}) \cdot \nabla \phi_\lambda(\mathbf{r}) d^3\mathbf{r} + \int v(\mathbf{r}) \phi_\kappa(\mathbf{r}) \phi_\lambda(\mathbf{r}) d^3\mathbf{r}, \quad (7)$$

$$(\kappa\lambda|\mu\nu) = \int \phi_\kappa(\mathbf{r}) \phi_\lambda(\mathbf{r}) |\mathbf{r} - \mathbf{r}'|^{-1} \phi_\mu(\mathbf{r}') \phi_\nu(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}', \quad (8)$$

whereas in the scalar-relativistic approximation based on an exact separation of spin-dependent terms of the Dirac–Coulomb Hamiltonian [6] they become

$$s_{\kappa\lambda} = \int \left(\phi_\kappa^0(\mathbf{r}) \phi_\lambda^0(\mathbf{r}) + \frac{1}{4c^2} \nabla \phi_\kappa^1(\mathbf{r}) \cdot \nabla \phi_\lambda^1(\mathbf{r}) \right) d^3\mathbf{r}, \quad (9)$$

$$h_{\kappa\lambda} = \frac{1}{2} \int \left(\nabla \phi_\kappa^0(\mathbf{r}) \cdot \nabla \phi_\lambda^0(\mathbf{r}) + \nabla \phi_\kappa^1(\mathbf{r}) \cdot \nabla \phi_\lambda^0(\mathbf{r}) - \nabla \phi_\kappa^1(\mathbf{r}) \cdot \nabla \phi_\lambda^1(\mathbf{r}) \right) d^3\mathbf{r} + \int v(\mathbf{r}) \left(\phi_\kappa^0(\mathbf{r}) \phi_\lambda^0(\mathbf{r}) + \frac{1}{4c^2} \nabla \phi_\kappa^1(\mathbf{r}) \cdot \nabla \phi_\lambda^1(\mathbf{r}) \right) d^3\mathbf{r}, \quad (10)$$

$$(\kappa\lambda|\mu\nu) = \int \left(\phi_\kappa^0(\mathbf{r}) \phi_\lambda^0(\mathbf{r}) + \frac{1}{4c^2} \nabla \phi_\kappa^1(\mathbf{r}) \cdot \nabla \phi_\lambda^1(\mathbf{r}) \right) |\mathbf{r} - \mathbf{r}'|^{-1} \times \left(\phi_\mu^0(\mathbf{r}') \phi_\nu^0(\mathbf{r}') + \frac{1}{4c^2} \nabla \phi_\mu^1(\mathbf{r}') \cdot \nabla \phi_\nu^1(\mathbf{r}') \right) d^3\mathbf{r} d^3\mathbf{r}', \quad (11)$$

where $\phi_\kappa^0(\mathbf{r})$ and $\phi_\kappa^1(\mathbf{r})$ are the spatial parts of the large component and of the transformed small component. In the non-relativistic limit

$$\lim_{c \rightarrow \infty} \phi_\kappa^1(\mathbf{r}) = \phi_\kappa^0(\mathbf{r}). \quad (12)$$

The potential $v(\mathbf{r})$ in (7) is taken to be that of a point nucleus, whereas Gaussian nuclear charge distributions with parameters from [7] are adopted for $v(\mathbf{r})$ in (10).

2.2. Low-lying excited configurations

A required number of basis functions K_l (for each angular quantum number l) for describing low-lying excited configurations of valence or Rydberg type can be added to the minimal Hartree–Fock set by diagonalizing the α -spin Fock matrix of an ionized system

$$f_{ab}^+ = \epsilon_a \delta_{ab}, \quad (13)$$

$$f_{ab}^+ = h_{ab} + (ab|ii)(w_{ix}^+ + w_{i\beta}^+) - (ai|ib)w_{ix}^+ \quad (14)$$

in the virtual subspace of the reference problem. The occupation numbers w_{ix}^+ , $w_{i\beta}^+$ correspond to an average of configurations with one electron removed out of the shell with the largest principal quantum number n and with the largest angular quantum number for that n . The occupied wavefunctions $\phi_i(\mathbf{r})$ in (14) come unchanged from the neutral system.

2.3. Intra- and inter-shell correlation

For an accurate description of electron correlation a large enough set of functions should be generated in addition to those described above. The way these functions are determined is a special characteristic of our approach. Second-order Møller–Plesset (MP2) perturbation theory [8] is the simplest treatment of electron correlation starting from the Hartree–Fock reference. The correlation energy expression for the closed-shell case

$$E_2 = \frac{(ai|bj)[2(ai|bj) - (bi|aj)]}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (15)$$

where the virtual part of the Fock matrix is assumed diagonal,

$$f_{ab} = \epsilon_a \delta_{ab}, \quad (16)$$

$$f_{ab} = h_{ab} + (ab|ii) - \frac{1}{2}(ai|ib) \quad (17)$$

can be defined also for a finite number N_{virt} of wavefunctions $\phi_a(\mathbf{r})$. An optimal set of such functions is required to minimize the expression (15) subject to orthogonality constraints and conditions (16). The numerator in (15) favors localization of $\phi_a(\mathbf{r})$ in the same region of space, where $\phi_i(\mathbf{r})$ are localized, whereas the denominator prevents them from having a too high kinetic energy. This property of the functional (15) can be used to contract the functions from the virtual space (which form a continuum spectrum for neutral atoms) to a limited number of well-behaved localized functions. This functional can be generalized for use

with any reference set of functions $\phi_i(r)$ (with energies ϵ_i) to generate a set of correlating functions. For atoms having open-shell configuration we redefine (17) as

$$f_{ab} = h_{ab} + w_i[(ab|ii) - \frac{1}{2}(ai|ib)], \quad (18)$$

where w_i are the same as in the reference expression (1).

Based on this idea, the last steps of our procedure are as follows. The combined set of functions of Sections 2.1 and 2.2 with the energies defined in (3) and (13) is now treated as if it were a set of occupied wavefunctions of a (fictitious) closed-shell atom. For each principal quantum number $n = n_{\max}, \dots, 1$ starting from the largest in this set the virtual wavefunctions are generated to represent intra-shell correlation for $n_i, n_j = n$ and inter-shell correlation for $n_i = n$ and all $n_j > n$ (n_i denotes the principal quantum number of ϕ_i). These functions are required to minimize (15), with i, j restricted to the selected subset, subject to proper orthogonality constraints and conditions (16) and (18). The number of radial functions for angular quantum number l added in this step is given by

$$N_{ln} = \max(0, A_n - \max(0, l - L_n - 1)), \quad (19)$$

where the integer A_n is the cardinal number of the basis set for the principal quantum number n , and L_n is the largest occupied angular quantum number for that n . One has thus a flexible choice of the number of functions added for correlating electrons in occupied shells with different n .

Special care should be taken to account for the fact that the condition (16) leads to a mixing of the functions being added for the given n with those already present in the virtual space. We have implemented a quadratically-convergent minimization algorithm for the determination of the correlating wavefunctions of this type within a finite primitive basis.

3. Gaussian expansions

The procedure outlined above can be used to produce general contractions of primitive sets of Gaussian functions for efficient molecular calculations. We have also developed a special approach for generating the primitive

sets in which the energy of a model independent-particle system

$$\tilde{E}_0 = \langle \tilde{\phi}_i | \hat{h}_0 | \tilde{\phi}_i \rangle, \quad (20)$$

is minimized with respect to the parameters of the approximate wavefunctions

$$\tilde{\phi}_i(\mathbf{r}) = c_{\mu i} Y_{l_i m_i}(\mathbf{r}/r) r^{l_i} \exp(-a_{\mu} r^2) \quad (21)$$

subject to proper orthogonality constraints. A common set of exponents a_{μ} is used for all angular momenta l_i in the relativistic case the expansion (21) is applied to both $\phi_i^0(\mathbf{r})$ and $\phi_i^1(\mathbf{r})$ using different coefficients $c_{\mu i}^0$ and $c_{\mu i}^1$. The Hamiltonian in (20) is defined in terms of its eigenfunctions

$$\hat{h}_0 = |\phi_{\kappa}\rangle \epsilon_{\kappa} \langle \phi_{\kappa}| \quad (22)$$

of which the first ϕ_{κ} are the exact (or highly accurate) occupied solutions from the problem (1) with the energies (3), and the rest correspond to the bound and continuum spectrum of the Fock matrix (14) diagonalized in the virtual electronic subspace of the neutral system. In the relativistic case the positronic solutions are excluded from the sum in (22), which enables a stable optimization of the exponents a_{μ} . The sum over i in (20) runs over all functions of Sections 2.1 and 2.2 to be included in the target contracted basis. Because all $\tilde{\phi}_i$ in (20) are assigned unit occupation, the optimization leads to a balanced description of core, valence, and Rydberg shells.

To represent the spectrum of \hat{h}_0 to high accuracy, a truncated set of functions $\phi_{\kappa}(\mathbf{r})$ is obtained from atomic calculations within a very large Gaussian basis, the exponents of which form a geometric series

$$a_p = 2^{p/3}, \quad p = p_{\min}, \dots, p_{\max}. \quad (23)$$

For non-relativistic calculations the integers $p_{\min} = -60$, $p_{\max} = 225$ were chosen yielding a total of 286 radial functions for each angular symmetry, in the scalar-relativistic case a smaller range $p_{\min} = -60$, $p_{\max} = 100$ was found adequate thanks to the absence of the nuclear cusp. All atomic calculations are done in 256-bit precision.

After a primitive set is optimized, it is usually modified by removing some largest and smallest exponents for

Table 1
Example of a Gaussian basis for Lithium: $K_1 = 1$, $A_1 = 1$, $A_2 = 1$

n, l	1,0	2,0	2,1	3,0	3,1	3,2	4,0	4,1
ϵ_{nl}	-2.4777	-0.1963	-0.1286	0.2105	0.2023	0.2405	5.0908	5.1670
a_{μ}	$c_{\mu nl}$							
1359.12	0.0008	-0.0001		-0.0002			-0.0014	
203.971	0.0065	-0.0010		-0.0012			-0.0120	
46.4366	0.0327	-0.0052		-0.0076			-0.0619	
13.1156	0.1194	-0.0192	0.0008	-0.0188	-0.0013		-0.4142	0.1169
4.20014	0.3022	-0.0535	0.0040	-0.0860	-0.0028		-0.7893	0.5532
1.44518	0.4576	-0.0973	0.0124	-0.1092	-0.0278		0.6283	0.4696
0.52146	0.2379	-0.1437	0.0488	-0.4729	-0.0613	0.0233	0.8430	-0.0065
0.15965	0.0041	0.0931	0.2117	1.4505	-0.8216	0.3964	-0.5373	-0.1935
0.05524	0.0024	0.7427	0.5156	0.0118	-0.0651	0.6949	-0.1970	-0.0800
0.02066	-0.0006	0.2763	0.3841	-0.9930	0.8291		0.2813	0.1291

Numbers rounded to save space. The coefficients $c_{\mu nl}$ refer to normalized primitive functions.

$l > 0$ as long as this does not degrade the quality of the resulting contracted set. The final contraction is done by applying the method of Section 2 within that primitive basis. The whole procedure is illustrated by the example of a basis for Lithium in Table 1.

4. Molecular tests

A detailed study of convergence properties of the new basis sets will be reported elsewhere. Here, the closed-shell

diatomics are chosen for the benchmark tests. The lengths of Gaussian expansions are taken to be large enough to get the values accurate to all digits shown. Using the coupled-cluster method with single and double substitutions [9] the equilibrium geometries are optimized using analytic gradients as implemented in our parallelized computer code [10]. A smooth convergence to the basis set limit can be observed from the data in Table 2, both for valence-only and for full treatment of correlation. The results for Cu_2 in Table 3 demonstrate the consistency between the non-relativistic and scalar-relativistic approaches.

For N_2 molecule a comparison of Hartree–Fock and CCSD correlation energies computed with our basis sets and with cc-pVXZ and cc-pCVXZ is made in Table 4. The latter results are taken from [11] and have also been

Table 2
Nonrelativistic CCSD calculations of diatomic molecules

Mol.	A_n	r	E	ΔE
H_2	1	1.41485	−1.16888	
	2	1.40736	−1.17239	
	3	1.40251	−1.17377	
	4	1.40134	−1.17416	
	5	1.40130	−1.17432	
	6	1.40122	−1.17438	
N_2	0,1	2.0745	−109.2994	0.3027
	0,2	2.0706	−109.3673	0.3297
	0,3	2.0661	−109.3860	0.3387
	0,4	2.0638	−109.3937	0.3431
	0,5	2.0634	−109.3968	0.3448
	1,1	2.0680	−109.3905	0.3086
	2,2	2.0639	−109.4771	0.3330
	3,3	2.0607	−109.5015	0.3416
	4,4	2.0596	−109.5100	0.3447
5,5	2.0591	−109.5139	0.3463	
Li_2	1,1	5.0860	−14.9763	0.03689
	2,2	5.0688	−14.9881	0.03785
	3,3	5.0614	−14.9914	0.03807
	4,4	5.0598	−14.9928	0.03812
	5,5	5.0591	−14.9933	0.03815
F_2	0,1	2.7393	−199.1975	0.0258
	0,2	2.6477	−199.3098	0.0398
	0,3	2.6304	−199.3477	0.0455
	0,4	2.6256	−199.3613	0.0476
	0,5	2.6238	−199.3671	0.0484
	1,1	2.7306	−199.2889	0.0265
	2,2	2.6404	−199.4297	0.0402
	3,3	2.6245	−199.4742	0.0457
	4,4	2.6211	−199.4894	0.0474
	5,5	2.6188	−199.4961	0.0483

Bond lengths, r , total energies, E , and atomization energies, ΔE (without vibrational contributions) in atomic units. $K_l = 0$ everywhere except $K_1 = 1$ for Lithium. For $A_1 = 0$ the 4 core electrons are not correlated.

Table 4

Hartree–Fock and CCSD correlation energies for N_2 molecule computed with the basis sets of the present work and with the cc-pVXZ [2] and cc-pCVXZ [3] sets

Set	N	E_0	E_c
$\Lambda 01$	14	−108.9737	−0.3256
cc-pVDZ	14	−108.9541	−0.3093
$\Lambda 02$	30	−108.9890	−0.3784
cc-pVTZ	30	−108.9835	−0.3719
$\Lambda 03$	55	−108.9907	−0.3953
cc-pVQZ	55	−108.9911	−0.3931
$\Lambda 04$	91	−108.9924	−0.4013
cc-pV5Z	91	−108.9928	−0.4006
$\Lambda 05$	140	−108.9928	−0.4039
cc-pV6Z	140	−108.9931	−0.4037
$\Lambda 11$	18	−108.9785	−0.4120
cc-pCVDZ	18	−108.9549	−0.3878
$\Lambda 22$	43	−108.9906	−0.4863
cc-pCVTZ	43	−108.9844	−0.4782
$\Lambda 33$	84	−108.9921	−0.5093
cc-pCVQZ	84	−108.9913	−0.5071
$\Lambda 44$	145	−108.9926	−0.5172
cc-pCV5Z	145	−108.9928	−0.5167
$\Lambda 55$	230	−108.9930	−0.5207
cc-pCV6Z	230	−108.9931	−0.5206

The bond length is fixed at 109.77 pm. Number of functions per atom N , Hartree–Fock E_0 and correlation E_c energies in atomic units.

Table 3
CCSD calculations of Cu_2 molecule with 38 correlated electrons

A_n	Non-relativistic				Scalar-relativistic			
	r	E	E_c	ΔE	r	E	E_c	ΔE
0,0,1,1	4.4066	−3279.2486	−1.3157	0.0629	4.3343	−3308.1960	−1.3264	0.0663
0,0,2,2	4.3488	−3279.6796	−1.7367	0.0602	4.2797	−3308.6275	−1.7488	0.0639
0,0,3,3	4.3225	−3279.8423	−1.8983	0.0599	4.2542	−3308.7901	−1.9103	0.0637
0,0,4,4	4.3081	−3279.9111	−1.9671	0.0601				

Bond length, r , total energy, E , correlation energy, E_c , and atomization energy, ΔE with respect to atoms in ^2S state (without vibrational contributions) in atomic units. The basis is generated for $3d^9 4s^2$ configuration (^2D state) of Copper atom, $K_1 = 1$.

Table 5
Non-relativistic CCSD calculations of CaO molecule with 16 correlated electrons

Set (Ca, O)	N	r	E_0	E_c	ΔE	Dipole	$-V/T$
$\Lambda 0011, \Lambda 01$	31, 14	3.6997	-751.5328	-0.4571	0.0529	3.017	1.999955
$\Lambda 0022, \Lambda 02$	63, 30	3.4804	-751.5825	-0.5627	0.1064	3.745	1.999942
$\Lambda 0033, \Lambda 03$	113, 55	3.4363	-751.5926	-0.6085	0.1268	3.805	2.000018
$\Lambda 0044, \Lambda 04$	185, 91	3.4118	-751.5959	-0.6262	0.1357	3.797	1.999987
$\Lambda 0055, \Lambda 05$	283,140	3.4078	-751.5965	-0.6336	0.1383	3.802	1.999994

Number of functions N for each atom. $K_n = 0$ everywhere except $K_1 = 1$ for Calcium. Bond length, r , Hartree–Fock E_0 and correlation E_c energies, atomization energy, ΔE , and dipole moment in atomic units. Virial ratio $-V/T$ for CCSD.

reproduced with our code. Both sets contain identical number of functions for each angular symmetry, the difference being only in the radial parts. One can see a better performance of our sets at the beginning of the series, whereas essentially the same energies are obtained for the largest sets.

The results for CaO molecule in Table 5 show the advantage of our new approach over the ANO treatment [5], where the lack of functions with certain radial extent was responsible for the poor prediction of the equilibrium bond length and other properties. Several visualization tools [12–14] have recently been suggested for getting a better insight into the deficiencies of a one-electron basis in such situations.

5. Conclusions

The new approach to the basis set generation presented here can be applied to any atom of the periodic table within non-relativistic as well as scalar-relativistic formalisms. Its extension for the spin–orbit coupled Dirac–Coulomb Hamiltonian is straightforward and will be reported separately. Test calculations show a smooth convergence of the computed molecular properties with the size of the basis. The possibility of basis set extrapolation [11,15,16] is to be

explored, as well as detailed calibration studies on various molecular systems (including excited states, anions and weakly-bound complexes) are to be performed, in the future.

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