

TOWARDS UNIVERSAL R12 CONSISTENT BASIS SETS

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

Using H^- and H_2 as examples, it is demonstrated that parameters of the one-electron basis sets optimized for explicitly correlated R12 calculations are quite different from those developed for conventional calculations that utilize a usual configuration interaction expansion for the wavefunction. Systematic development of universal R12 suited basis sets is suggested, using the even-tempered paradigm. In explicitly correlated calculations, such R12 consistent basis sets should describe the given atom in a variety of bonding situations with a few μE_h absolute accuracy.

Keywords: Electron correlation; Universal basis set; Explicitly correlated wavefunctions; R12 ansatz; *Ab initio* calculations; MP2.

When the three celebrated scientists started their successful career, *ab initio* quantum chemistry (see, e.g., ref.¹) stood at the beginning of a great boom. At the same time it became clear that the one-electron approximation was unsatisfactory and methods to treat electron correlation effects^{2,3} started to be developed for large scale calculations. Inspired by the work of Čížek^{4,5} – now safely denoted as classic – early developments towards this goal in the then Czechoslovakia naturally used diagrammatic techniques in the derivation of working equations^{6,7}. The method of choice was the many-body perturbation theory (MBPT) and later the coupled cluster (CC) theory. First applications were devoted to ionization potentials, electron affinities^{8–10}, excitation energies¹¹ and correlation energy to the third order of MBPT¹².

What we can now call the “conventional” *ab initio* approach relies upon the expansion of the final wavefunction in terms of configuration functions (CF) created as antisymmetrized product functions of certain type of one-electron spin-orbitals. These in turn are obtained within a one-electron approximation, usually as linear combinations of the given one-electron (computational) basis functions¹. All possible CF's form a complete configuration space. MBPT and CC theories provide alternative logical hierarchies towards the full configuration interaction (CI) (see, *e.g.*, ref.¹³). In the computational basis the full CI approach is an exact method when the wavefunction is expanded in a complete configuration space, and it is variationally determined. Unfortunately, by far this does not imply that the result itself is accurate in the full-CI limit. The choice of the one-electron basis is crucial, since the convergence of desired calculated properties with respect to the basis set size is frustratingly slow, even for “optimal” sets. In order to reach a few microhartree accuracy for the energy of the simple two-electron helium atom, the highest angular momentum quantum number (L) included in the basis^{14,15} should be $L > 10$. The calculation of ground-state energies for small many-electron few-atom molecules with an accuracy of *sub*-millihartree level *via* conventional configuration expansion is practically an unrealistic task. In fact, according to the analysis of partial-wave expansion of the He ground state, the basis set error goes as^{16,17} $\approx (L + 1)^{-3}$. Such a dependence applies both for variational and perturbational calculations and also for atoms other than He¹⁸.

Certainly, the basis set should be able to describe the electron density in space adequately. For one-electron approximation, this means to provide appropriate (possibly nearly optimal) spin-orbitals. Nowadays, for small molecules, calculations with basis sets saturated in this sense (nearly the Hartree–Fock limit) are feasible.

However, the mentioned slow convergence of CI with L is caused by a different problem. The origin of this problem is attributed to the poor description of the Coulomb hole. As shown by Kato¹⁹ for small interelectron distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$, the exact wavefunction behaves as:

$$\left\{ \frac{\partial \Psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_n)}{\partial r_{ij}} \right\}_{\vec{r}_i = \vec{r}_j} = \frac{1}{2} \Psi(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_n). \quad (1)$$

Within the approximate solutions of the Schrödinger equation through expansion in an orbital basis the correlation cusp cannot be reproduced. Similarly to two electrons, the wavefunction has also a cusp at the position of

the nucleus. Again, using the computationally pragmatic Gaussian basis sets²⁰, this behavior cannot be described. However, the error introduced by this defect is much smaller and converges rather fast with the dimension (N) of the (atom-centered) basis set as²¹ $\sim AN^k \exp(-a\sqrt{N})$. A , k , and a are parameters.

There are most probably hundreds of papers dealing with the basis set construction and improvements. Early development was reviewed in the second chapter of the book by Čársky and Urban¹, or, *e.g.*, in refs^{22,23}. This problem was also a topic of the early work of our celebrated persons²⁴⁻³⁰.

In the present paper we shall consider basis sets from the viewpoint of wavefunction expansions that go beyond the "conventional" ones as the aforementioned. We shall discuss explicitly correlated expansions that *a priori* treat the correlation cusp *via* the introduction of terms explicitly depending on r_{ij} .

First, we briefly recapitulate the theory. Further, using hydrogen as an example, we illustrate how the optimal one-electron basis set must be changed if one switches from conventional to explicitly correlated expansions. We show that within the explicitly correlated approach basis sets that should work universally with high precision for a range of bonding situations are feasible.

THEORY

The R12 Approach

Long ago it was observed that inclusion of terms linear in r_{12} in the wavefunction expansion speeded up the convergence of helium ground state tremendously³¹. Hylleraas^{31,32} suggested expanding the final wavefunction in a series of CI-type expansions associated with various odd powers of r_{12} . Though not difficult to apply to two-electron systems, such an approach becomes impractical as soon as more electrons are involved. The reason is simply that an interaction of the two-electron r_{ij} with the two-electron Hamiltonian gives rise to a four electron operator, in general. Consequently, the amount of integrals to be treated becomes too large. Moreover, such integrals are difficult to calculate.

There is another concept that goes *a priori* beyond the orbital expansion – it is based upon a direct expansion of the wavefunction both in terms of one- and two-particle Gaussian type functions^{33,34} which are variationally optimized. Similarly to one-particle Gaussians, the integrals with explicitly correlated two-particle Gaussian functions are not difficult to calculate.

Nevertheless, an enormous number of integrals remains, and nonlinear parameters of these functions have to be optimized for each system. In spite of successful implementations within the coupled cluster ansatz that enabled treatment of larger than four-electron systems^{35,36}, this concept most probably remains feasible for small systems only. For up to four-electron systems, extremely accurate results can also be obtained with exponentially correlated Gaussians³⁷.

A family of approaches denoted as R12 methods is based on the fact that in order to satisfy the cusp condition (1) it is sufficient to introduce terms linear in r_{12} to an orbital product expansion^{17,38}. Though originally Kutzelnigg applied the R12 ansatz to helium, this ansatz can be simply generalized. Let us introduce the operator

$$\hat{r} = \sum_{p>q} r_{pq}. \quad (2)$$

According to Kutzelnigg³⁸, the exact wavefunction (Ψ) can be appropriately described as:

$$|\Psi\rangle = \frac{1}{2} \hat{r} |\Phi\rangle + |\chi\rangle, \quad (3)$$

where Φ is a “conventional” reference function resulting from the solution within a one-electron approximation and χ is a “conventional” CI-type expansion. Ansatz of Eq. (3) itself would not solve the problem of many-electron integrals. In order to arrive at an approach in which those can be avoided, one needs further considerations.

There is a substantial overlap between $\hat{r}\Phi$ and χ that is undesirable. In other words, from $\hat{r}\Phi$ it is desirable to out-project the content expressible in the given one-electron basis. To simplify, let us assume that Φ is a single Slater determinant. Let φ_i, φ_j , etc. be occupied spin-orbitals and φ_p, φ_q , etc. denote arbitrary spin-orbitals of the given computational basis. We can define a projector to this basis

$$\hat{P}_1 = \sum_p |\varphi_p\rangle\langle\varphi_p|. \quad (4)$$

In Φ , the operator r_{12} acts on pair products of occupied spin-orbitals. The afore-mentioned out-projecting for an antisymmetrized product function

$$|ij\rangle = \frac{1}{\sqrt{2}}|\varphi_i\varphi_j - \varphi_j\varphi_i\rangle = \frac{1}{\sqrt{2}}\{\varphi_i(1)\varphi_j(2) - \varphi_j(1)\varphi_i(2)\} \quad (5)$$

means that we have

$$\hat{Q}_{12}r_{12}|ij\rangle = (1 - \hat{P}_1)(1 - \hat{P}_2)r_{12}|ij\rangle. \quad (6)$$

Here we have introduced \hat{Q}_{12} as a two-particle projector to the basis complementary to the given computational one. In fact, by the action of $\hat{Q}_{12}r_{12}$ on $|ij\rangle$, one replaces the pair function $|ij\rangle$ by the same pair function multiplied by r_{12} . More generally, in $|\Phi\rangle$ one can replace $\varphi_i(1)\varphi_j(2)$ by an arbitrary product $r_{12}\varphi_k(1)\varphi_l(2)$. Thus we can define a replacement operator \hat{R}_{ij}^{kl} by

$$\hat{R}_{ij}^{kl}|ij\rangle = \hat{Q}_{12}r_{12}|kl\rangle. \quad (7)$$

Such replacement can be denoted as r_{12} -double excitation. Now, instead of a fixed factor $1/2$ in Eq. (3), we can associate a scalar coefficient c_{kl}^{ij} with each \hat{R}_{ij}^{kl} . These operator amplitudes are determined similarly to those associated with the “conventional” configuration functions. The total r_{12} -double excitation operator is then given by:

$$\hat{R} = \sum_{\substack{i>j \\ k>l}} c_{kl}^{ij} \hat{R}_{ij}^{kl}. \quad (8)$$

Hence, by introducing $\hat{R}\Phi$ into the final wavefunction expansion, the configuration space is extended by r_{12} -double excitations. Methods using this ansatz – though sometimes with a slightly different projector – are in current literature denoted as R12 approaches. It is clear from Eq. (7) that such r_{12} -double excitations vanish in the case of complete one-electron basis.

First-order wavefunction in the Møller–Plesset R12 (MP2-R12) theory reads:

$$\Psi^{(1)} = \hat{R}^{(1)}\Phi + \chi^{(1)} = \sum_{\substack{i>j \\ k>l}} (c_{kl}^{ij})^{(1)} \hat{R}_{ij}^{kl}\Phi + \chi^{(1)}, \quad (9)$$

where $\chi^{(1)}$ is exactly the same as within the conventional MP2 theory. In first applications, c was restricted to diagonal c_{ij}^{ij} , which did not provide an

orbital invariant approach³⁹. Orbital invariant R12 approaches followed after introducing MP2-R12 with the full ansatz⁴⁰ in Eq. (9). Later, it was shown that in the coupled-cluster theory, the r_{12} -double-excitation operator can be treated together with the (conventional) global cluster excitation operator (\hat{T}), defining so the coupled cluster R12 (CC-R12) ansatz⁴¹⁻⁴³:

$$\Psi_{\text{CC-R12}} = \exp(\hat{R} + \hat{T})\Phi; \quad \hat{T} = \sum_n \hat{T}_n, \quad (10)$$

where \hat{T}_n is an n -tuple-excitation operator. With CC-R12 highly accurate results can be obtained as collected in a recent review by us⁴⁴. The main advantage of R12 approaches is that, formally, the expansion remains limited to a one-electron basis.

In working equations of all the R12 methods, avoiding of difficult many electron integrals is accomplished within the so-called “standard approximation”^{42,45}. The latter is based upon an elaborate use of completeness insertions, and upon using the favorable convergence pattern of the partial wave expansions of some “difficult” matrix elements. In approximation B, which is used in CC-R12, all the matrix elements are neglected that have a terminating ℓ expansion due to the symmetry, or for which the error of the ℓ expansion decreases as⁴⁵ $\sim O(L + 1)^{-7}$.

Beside the two mentioned explicitly correlated approaches, other variants were suggested that basically combine features of both the R12 ansatz and the explicitly correlated Gaussians: r_{12} is replaced by a fit of only few explicitly correlated Gaussians^{46,47}. A review of explicitly correlated methods can be found in ref.⁴⁸

R12 Approach and Basis Sets

Standard approximation turns to exact treatment for atoms, provided the basis set is well saturated at a certain level of lower angular momenta. Under the latter condition it is close to “exact” for molecules, too. Practically, this limitation means that saturation up to $L = 3L_{\text{occ}}$ is required, where L_{occ} corresponds to the highest angular momentum of the occupied orbitals. In addition, in CC-R12, all shells that are present in the computational basis set should be saturated^{42,43}. Though the latter condition follows from the theory, ten years of experience show that it is not a very strict requirement, since it concerns higher-order contributions. We have to note that for relevant calculations the R12 contributions of the same order – in the sense of

MBPT – are smaller by about two orders of magnitude than those being attributed to the conventional configuration space⁴⁴.

One of the reasons which imply saturation of the basis set is the requirement that the computational basis is large enough to substitute the resolution of identity. Under such assumption, one can factorize the three-electron integrals to products of two-electron integrals. Latest development at the MP2-R12 level shows that for this purpose an auxiliary basis can be introduced, and, in principle, the computational basis can be a standard one from conventional calculations⁴⁹. On the other hand, the same study indicates that in order to obtain highly accurate results that are expected from explicitly correlated calculations, the basis set has to be large. Eventually, the use of auxiliary basis with a little modified R12 ansatz provides a possibility of reducing the requirement for the L saturation to lower levels than $3L_{\text{occ}}$. Work along this line within the CC-R12 theory is in progress⁵⁰.

Most R12 calculations reported so far used very large conventionally optimized basis sets which were adapted in a heuristic fashion. Even if the saturation level could be decreased to $L = L_{\text{occ}}$, the standard approximation requirements imply that the basis sets should provide near Hartree–Fock limit energies at the one-electron approximation level. For first row atoms, high-quality 18s13p basis sets of this kind were developed by Partridge⁵¹. Those proved to be good outsets for constructing R12 reliable basis sets⁵². Adequate basis sets were often created from correlation consistent bases⁵³ with high cardinal numbers⁵⁴, either fully uncontracted or, better, with the sp set replaced by that of Partridge. In addition, both the sp and polarization sets were usually augmented by few diffuse or tight functions by mere logarithmic extrapolation^{55–59}.

Although such basis sets worked well, there are good reasons to look for improvements. One can certainly assume that optimization at the conventional niveau necessarily interferes with some partial compensation for the poor description of the electronic cusp. Hence, the range of exponents for the Gaussian functions may not be optimal for R12 calculations. Surely, this problem can be solved by augmenting the “conventional” sets, though any enlargement is undesirable from the computational point of view. Alternatively, it is likely that specifically R12-optimized bases could be either smaller for comparable quality, or would provide more accurate results than the aforementioned R12 variants of conventional sets.

OPTIMIZATION PROCEDURE

In order to explore the possibilities in this direction, we start with basis sets close to the HF limit, and focus on polarization functions only⁴⁴. Reducing the number of adjustable parameters is conveniently accomplished through using even-tempered sets^{60,61}. Here we shall define each set by the most compact exponent of the Gaussian function (α_{l_0}) and the progression ratio (β_l), which provides:

$$\alpha_{l_0} = \alpha_l \beta_l^i \quad \text{for } i = 0, \dots, n_l - 1, \quad (11)$$

where n_l is the number of functions in the given shell l .

Our objective is to find such basis sets that would be capable of describing different target systems with high (and similar) accuracy. Appropriate target systems are *e.g.* positively charged, neutral, negatively charged atoms and, eventually atoms under the influence of an external electric field. For the latter, the original symmetry of the atom is broken, thus simulating the situation in polar bonds. Similar target systems were used in developing the ANO basis sets by Widmark *et al.*⁶² Such optimization is in progress for atoms from Be to Ne, for polarization functions up to h, and will be published elsewhere⁶³.

In order to find the global "compromise" optimum for all the target systems and the polarization set given by l , we proceed as follows.

First, we calculate $E = E(\alpha_{l_0}, \beta_l)$ energy surfaces for individual target systems. In this step, the parameters for lower angular momenta are kept from previous optimization, or from the outset. It is not necessary to include higher angular momenta, if only this is not required by standard approximation. So, for instance, f functions must be present while d functions are optimized as soon as in any of the target systems p orbitals are occupied, but it is not necessary to include g functions while f set is optimized.

In the second step, we construct error maps for each target system that monitor the energy deviation for arbitrary α , β from the minimum on the $E(\alpha, \beta)$ surface.

Finally, a global error map is constructed. For the given α , β the largest of the errors out of all the target systems is taken as the global error value. The minimum on this global error map corresponds to globally optimal parameters α_{l_0} and β_l . These are then used in subsequent optimization of a higher l set.

A SIMPLE CASE – THE BASIS SET FOR HYDROGEN

In order to see whether the matter would be worth effort, we started with the basis set for hydrogen. Because H^+ and H atom are irrelevant target systems (with no electron correlation), we have investigated H^- and H_2 with a fixed bond length of $1.4 a_0$ that is close to equilibrium distance. These two systems have the advantage that the full-CI limit is achieved at the CCSD level. Thus within the CCSD-R12 theory with a large enough basis, calculated energies should come very close to exact values. Moreover, the standard approximation requirements are exactly fulfilled with saturation of s set for H^- , and practically also for H_2 . Consequently, we can start from a well saturated s set, and subsequently optimize p , d , f , *etc.* polarization sets with only a total sp , spd , $spdf$, *etc.* bases, respectively.

Our investigations used the aug-cc-pV5Z basis as a starting point. This set comprises $9s5p4d3f2g$ functions that are normally contracted to $6s5p4d3f2g$, *i.e.* 80 functions per H atom. For example, this size is needed to achieve an accuracy within few kJ/mol in thermochemistry of small hydrides by using conventional calculations and extrapolations⁶⁴. Fully uncontracted and augmented with one tight p ($\alpha = 11.9$) the $spdf$ subset (68 functions) has proved to be equally accurate in the calculations of atomization energies using the R12 theory⁵⁹, but with no extrapolations. We call this $9s6p4d3f$ as the “parent” basis here.

Our aim was to compare the trends when the basis set of this particular size is optimized for conventional and R12 calculations. Comprehensive results are collected in Table I. We have left the $9s$ set untouched from the parent basis. p , d , and f sets were optimized as described above. Results using the $9s6p$ subset from the parent basis and optimizing only d and f sets in ref.⁴⁴ were rather preliminary, but interesting enough to prompt further research in this direction that would also reinvestigate the $6p$ set.

The optimized $6p$ set (entry H^- , H_2) resulted from calculations with $9s6p$ set, $4d$ set from $9s6p4d$ calculations with the optimal $9s6p$ subset, and finally, while optimizing the $3f$ set we used the optimal $9s6p4d$ subset. This sequence has been performed separately using the R12 and “conventional” methods.

We have to note that the parameters in the entries for H^- and H_2 of Table I correspond to minimal energies of particular systems when the compiled optimum subset for lower angular momenta was used, *i.e.* these subsets are always the same for all the three lines (H^- , H_2 and $'H^-, H_2'$). For comparison, we display the energies and approximate parameters for the subsets of the parent basis. The latter is close to an even tempered series, and we can de-

TABLE I
Comparison of the parameters of the 9s6p4d3f basis and its subsets optimized for R12 and conventional calculations

Optimized for:	nl^a	α_{l_0}	$\alpha_{l_{n-1}}$	β_l	E_{H^-}/E_H	E_{H_2}/E_H	$\Delta E/\mu E_H^b$	
R12	H ⁻	6p	4.0	0.028	0.37	-0.5275685	-1.1741004	20
	H ₂		10.0	0.116	0.41	-0.5269457	-1.1741207	623
	H ⁻ , H ₂		5.0	0.035	0.37	-0.5275531	-1.1741051	15
conv.	H ⁻	6p	3.5	0.041	0.41	-0.5263656	-1.1722226	31
	H ₂		8.0	0.183	0.47	-0.5255418	-1.1722540	823
	H ⁻ , H ₂		4.5	0.066	0.43	-0.5263526	-1.1722368	17
R12	parent	6p	11.9	0.074	0.36	-0.5271560	-1.1741172	412
conv.						-0.5263420	-1.1722380	23
R12	H ⁻	4d	0.6	0.038	0.40	-0.5276599	-1.1743390	73
	H ₂		2.0	0.221	0.48	-0.5275881	-1.1744118	72
	H ⁻ , H ₂		1.4	0.065	0.36	-0.5276517	-1.1744050	8
conv.	H ⁻	4d	2.5	0.117	0.36	-0.5272154	-1.1738972	30
	H ₂		5.0	0.426	0.44	-0.5270723	-1.1739277	143
	H ⁻ , H ₂		3.5	0.192	0.38	-0.5272048	-1.1739140	14
R12	parent	4d	2.95	0.156	0.38	-0.5273878	-1.1744134	282
conv.						-0.5272041	-1.1739151	13
R12	H ⁻	3f	0.4	0.058	0.38	-0.5276732	-1.1744168	13
	H ₂		1.5	0.317	0.46	-0.5276543	-1.1744349	19
	H ⁻ , H ₂		1.0	0.090	0.30	-0.5276680	-1.1744298	5
conv.	H ⁻	3f	2.0	0.231	0.34	-0.5273862	-1.1741831	31
	H ₂		4.0	0.706	0.42	-0.5273440	-1.1742142	42
	H ⁻ , H ₂		3.0	0.347	0.34	-0.5273752	-1.1742047	11
R12	parent	3f	2.51	0.274	0.33	-0.5274743	-1.1744371	199
conv.						-0.5273836	-1.1741980	16

^a Subsets of 9s6p4d3f up to the given l . 9s taken from the parent set, the even-tempered nl set subsequently optimized within CCSD-R12 or conventional CCSD, as noted in the first column. For the parent basis set, the α and β parameters are approximate. Subsets are taken from the original parent set (see the text), and they are the same for both the R12 and conventional calculations. ^b For the given l , a maximum of the two deviations from the optimal values for individual systems.

termine approximate corresponding α and β parameters from the most diffuse and the most compact exponents of the original set using the formula

$$b_l^{n_l-1} = (\alpha_{l_{\text{diffuse}}} / a_{l_{\text{compact}}}). \quad (12)$$

The Range of Gaussian Exponents

One trend is clear for all the optimized sets, namely that the R12 suited bases are more diffuse than those optimized for conventional calculations. This statement is valid for individual target systems, as well as for the global optimum basis.

Concerning the range of exponents, an apparently different behavior is seen for the 6p set and for the higher polarization functions. While for 6p functions with explicitly correlated method the covered range of exponents was broader than with conventional approach, for 4d and 3f sets the opposite is true.

In fact, to localize the absolute minima for individual H^- and H_2 $\alpha_p - \beta_p$ surfaces is quite difficult, since there are several local minima that differ at the microhartree level. The parameters in Table I were estimated from a grid of 21×24 points with α in the range 2.5–12.5 by 0.5 steps and with β in the range 0.25–0.71 by 0.02 steps.

On the other hand, the occurrence of such almost equivalent local minima with very small barriers between them denotes a fair saturation of the given set for the given system. On the α - β map these minima are located along (almost) straight lines with different slopes for individual target systems. Consequently, the global optimal region for H^- and H_2 together can be clearly identified. In Table II we show the parameters that resulted from an optimization of 7p functions with the same 9s set. Surprisingly, on the very flat surface for H_2 the apparent minima correspond to smaller α_0 values than for 6p for both the R12 and conventional calculations. Nevertheless, parameters for the common optimum behave as expected, *i.e.* the range covered by the exponents is broadened. Actually, the compiled 7p basis is close to a simple extension of the 6p set by one more compact function. This addition brings about the same (tiny) effect at both conventional and R12 levels. Thus, from the point of view of various calculated properties, the 6p set seems to be, as stated above, saturated enough.

The p set is the most important polarization set to describe the dynamic electron correlation. Because of the fair saturation the differences in the

covered exponent ranges for the R12-optimized and conventional sets are quite small. The slightly denser mesh of functions in conventional sets results from the need to describe the electronic cusp through an expansion in the given basis set, whereas in R12 calculations this is done through explicit introduction of the r_{12} into the wavefunction. Consequently, the full "power" of the 6p set is released, enabling a better spatial covering, corresponding to the broader p exponent range.

For the same reason, the R12-optimized 4d and 3f sets tend to prefer the diffuse regions, while in conventional bases much more compact functions are optimal.

Individual and Global Optima

An example for the different pattern of the energy error contour maps from R12 and conventional optimizations is demonstrated by Figs 1 and 2 for the d functions. It is characteristic that in the case of R12 basis the two minima (for H^- and H_2) are much closer to each other than for the conventional one. Consequently, the error of the global basis set with respect to the two minima is lowered by about a factor of two, for both 4d and 3f sets (*cf.* Table I). In Fig. 3 we compare the global error maps from R12 and conventional optimization. For the given angular momentum, the contours limit the regions where the basis sets defined by any α , β coordinates are reliable within the given global error. The broader limits in R12 calculations are obvious. Note that in conventional map the contour for $10 \mu E_h$ is missing, since the smallest error exceeds this limit.

TABLE II

Parameters of the 7p even tempered set of the 9s7p basis for hydrogen as optimized for conventional and R12 calculations. 9s set is the same as in Table I

Optimized for:		α_{I_0}	α_{I_6}	β_I	E_{H^-}/E_h	E_{H_2}/E_h	$\Delta E/\mu E_h^b$
R12	H^-	6.0	0.029	0.41	-0.5275724	-1.1741086	17
	H_2	8.0	0.086	0.47	-0.5271408	-1.1741251	432
	H^-, H_2	12.5	0.032	0.37	-0.5275652	-1.1741158	9
conv.	H^-	5.0	0.032	0.43	-0.5263693	-1.1722376	20
	H_2	7.0	0.155	0.53	-0.5259441	-1.1722579	425
	H^-, H_2	9.0	0.057	0.43	-0.5263624	-1.1722510	7

^a Error as defined in Table I.

From Figs 1–3, one can clearly see that the global R12-optimized basis is more universal in R12 calculations than its conventional counterpart in

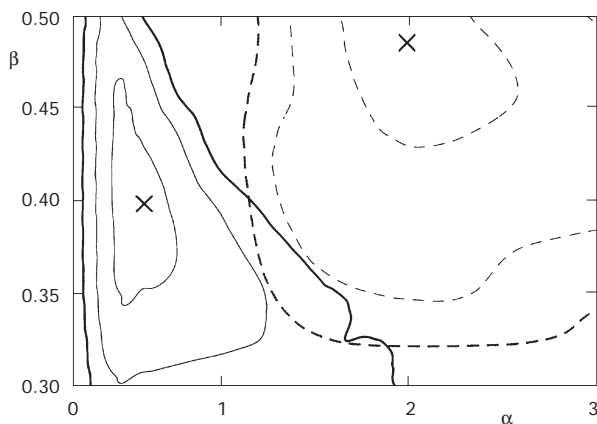


FIG. 1

Error contour maps from $E = E(\alpha_d, \beta_d)$ 9s6p4d CCSD-R12 energy surfaces of H_2 (solid) and H^- (dashed). Contours correspond to errors of 1, 5 and 10 (thick) μE_h with respect to the minima of the respective energy surfaces whose locations are denoted by the crosses. The 9s6p subset was R12-optimized as described in Table I

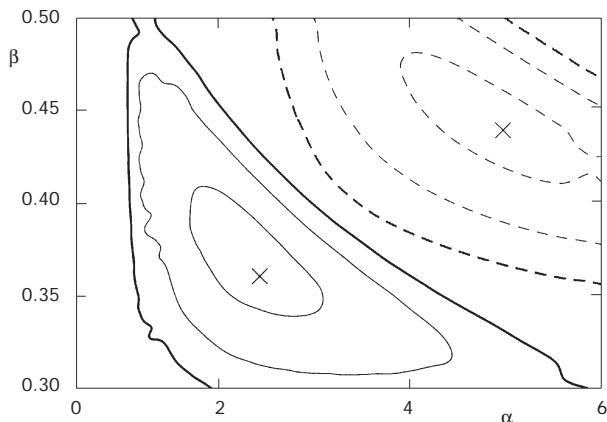


FIG. 2

Error contour maps from $E = E(\alpha_d, \beta_d)$ 9s6p4d CCSD energy surfaces of H_2 (solid) and H^- (dashed). Contours correspond to differences of 1, 5 and 10 (thick) μE_h with respect to the minimum of the energy surface. The 9s6p subset was optimized using conventional approach (see Table I)

conventional calculations. The wide range of α and β parameters for which the global error remains rather small supports the statement that the polarization sets for R12 calculations can be safely even-tempered, irrespective of the small number of functions in them.

Errors and Consistency

The last columns in Tables I and II demonstrate the limiting errors in the energies calculated with the given polarization set as compared to sets optimized for individual molecules. The H^- entry indicates the error for H_2 using the polarization set optimal for H^- and *vice versa* for the entry H_2 . Finally, the entry ' H^-, H_2 ' corresponds to the larger of both errors for the globally optimal polarization set. The same applies to the parent basis. We could say that the set is internally consistent if this error is close to zero.

It is not surprising that the error for H^- is very large if calculated with functions that are optimal for H_2 . This is equally valid for R12 and conventional calculations. Our results also show that the parent basis, which was basically optimized for conventional calculations, performs only slightly worse than sets optimized for conventional calculations. On the other hand, R12 results with the parent set clearly show that bases well suited for

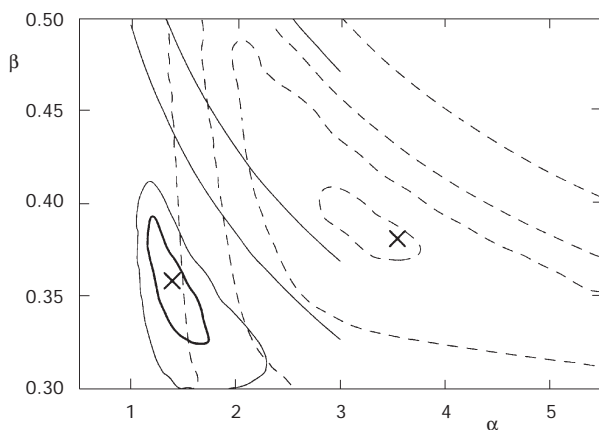


FIG. 3

Global error contour maps from $E = E(\alpha_d, \beta_d)$ 9s6p4d energy surfaces of H_2 and H^- . Solid lines correspond to CCSD-R12 optimized sets (see Fig. 1) and dashed lines to conventional CCSD optimized sets (see Fig. 2). Crosses denote the positions of the minimum errors (see Table I). Contours cover areas with maximum errors up to $10 \mu E_h$ (thick line for R12 only), 15, 30, 50, and $100 \mu E_h$ (thin lines for both cases)

conventional calculations can fail in R12. The parent basis was rather inconsistent for R12 calculations, providing a big consistency error of about $200 \mu E_h$ for H^- with 9s6p4d3f set and still more when only its subsets were used. However, the global R12-optimized basis provides a consistency error of only a few μE_h for each polarization set.

CONCLUSIONS

We have shown that basis sets optimized for conventional calculations are far from being optimal in explicitly correlated R12 approaches. On the examples of H^- and H_2 we have demonstrated that the standard practice of using uncontracted "conventional" sets subsequently augmented in the tight and diffuse region, though acceptable for some particular systems, may be inadequate for others. If one is seeking a universal predictive power, such bases are inappropriate.

As our results show, the simple even-tempered paradigm works well (at least for the large basis sets needed in highly accurate calculations) and can be used for a systematic development of R12-suited universal basis sets. Without any change, those could be used for atoms in various bonding situations, basically preserving the absolute accuracy achievable at the R12 level. The optimization procedure consists in finding the minimum error region on the overlapping α - β maps for few different atomic systems that cover the spectrum of all possible bonding situations. This is done for each polarization set separately, while the sets for lower angular momenta should closely provide the Hartree-Fock limit at one-electron approximation level.

As an additional benefit, our preliminary compilations also indicated that such optimization procedures may lead to basis sets intrinsically free from numerical instabilities occurring from time to time in R12 calculations^{44,65}.

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REFERENCES

1. Čárský P., Urban M.: *Ab Initio Calculations. Methods and Applications in Chemistry*, Lecture Notes in Chemistry, Vol. 16. Springer Verlag, Berlin, 1980.
2. Löwdin P. O.: *Adv. Chem. Phys.* **1959**, 2, 207.

3. Čársky P., Hubač I.: *Chem. Listy* **1977**, 71, 673.
4. Čížek J.: *J. Chem. Phys.* **1966**, 45, 4256.
5. Čížek J.: *Adv. Chem. Phys.* **1969**, 14, 35.
6. Paldus J., Čížek J.: *Adv. Quantum Chem.* **1975**, 9, 105.
7. Hubač I., Čársky P.: *Top. Curr. Chem.* **1978**, 75, 97.
8. Hubač I., Kvasnička V., Holubec A.: *Chem. Phys. Lett.* **1973**, 23, 381.
9. Kvasnička V., Hubač I.: *J. Chem. Phys.* **1974**, 60, 4483.
10. Hubač I., Urban M.: *Theor. Chim. Acta* **1977**, 45, 185.
11. Kvasnička V., Holubec A., Hubač I.: *Chem. Phys. Lett.* **1974**, 24, 361.
12. Urban M., Kellö V., Hubač I.: *Chem. Phys. Lett.* **1977**, 51, 170.
13. Urban M., Černušák I., Kellö V., Noga J. in: *Method in Computational Chemistry* (S. Wilson, Ed.), Vol. I, p. 117. Plenum Press, New York 1987.
14. Bunge C. F.: *Theor. Chim. Acta* **1970**, 16, 126.
15. Carroll D. P., Silverstone H. J., Metzger R. M.: *J. Chem. Phys.* **1979**, 71, 4142.
16. Schwartz C.: *Phys. Rev.* **1962**, 126, 1015.
17. Hill R. N.: *J. Chem. Phys.* **1985**, 83, 1173.
18. Kutzelnigg W., Morgan J. D.: *J. Chem. Phys.* **1992**, 96, 4484.
19. Kato T.: *Commun. Pure Appl. Math.* **1957**, 10, 151.
20. Boys S. F.: *Proc. R. Soc. London, Ser. A* **1950**, 200, 542.
21. Kutzelnigg W.: *Int. J. Quantum Chem.* **1994**, 51, 447.
22. Huzinaga S.: *Comput. Phys. Rep.* **1985**, 2, 279.
23. Wilson S. in: *Ab Initio Methods in Quantum Chemistry* (K. P. Lawley, Ed.), p. 439. Wiley, New York 1987.
24. Urban M.: *Chem. Listy* **1971**, 65, 690.
25. Urban M.: *Collect. Czech. Chem. Commun.* **1971**, 36, 3482.
26. Urban M.: *Collect. Czech. Chem. Commun.* **1973**, 38, 2043.
27. Urban M., Polák R.: *Collect. Czech. Chem. Commun.* **1974**, 39, 2567.
28. Urban M., Kellö V., Čársky P.: *Theor. Chim. Acta* **1977**, 45, 205.
29. Urban M., Pavlík S., Kožár T.: *Chem. Zvesti* **1977**, 31, 165.
30. Čársky P., Kozák I., Kellö V., Urban M.: *Collect. Czech. Chem. Commun.* **1977**, 42, 1460.
31. Hylleraas E. A.: *Z. Phys.* **1929**, 54, 347.
32. Hylleraas E. A.: *Adv. Quantum Chem.* **1964**, 1, 1.
33. Boys S. F.: *Proc. R. Soc. London, Ser. A* **1960**, 258, 402.
34. Singer K.: *Proc. R. Soc. London, Ser. A* **1960**, 258, 412.
35. a) Szalewicz K., Jeziorski B., Monkhorst H. J., Zabolitzky J. G.: *J. Chem. Phys.* **1983**, 78, 1420; b) Szalewicz K., Jeziorski B., Monkhorst H. J., Zabolitzky J. G.: *J. Chem. Phys.* **1983**, 79, 5543.
36. Bukowski R., Jeziorski B., Szalewicz K.: *J. Chem. Phys.* **1999**, 110, 4165.
37. Rychlewski J.: *Adv. Quantum Chem.* **1998**, 31, 173.
38. Kutzelnigg W.: *Theor. Chim. Acta* **1985**, 68, 445.
39. Klopper W., Kutzelnigg W.: *Chem. Phys. Lett.* **1986**, 134, 17.
40. Klopper W.: *Chem. Phys. Lett.* **1991**, 186, 583.
41. Noga J., Kutzelnigg W., Klopper W.: *Chem. Phys. Lett.* **1992**, 199, 497.
42. Noga J., Kutzelnigg W.: *J. Chem. Phys.* **1994**, 101, 7738.
43. Noga J., Klopper W., Kutzelnigg W. in: *Recent Advances in Coupled-Cluster Methods, Recent Advances in Computational Chemistry* (R. J. Bartlett, Ed.), Vol. 3, p. 1. World Scientific, Singapore 1997.

44. Noga J., Valiron P. in: *Computational Chemistry: Reviews of Current Trends* (J. Leszczynski, Ed.), Vol. 7, p. 131. World Scientific, Singapore 2002.
45. Kutzelnigg W., Klopper W.: *J. Chem. Phys.* **1991**, *94*, 1985.
46. Taylor P. R., Persson B. J.: *J. Chem. Phys.* **1996**, *96*, 5915.
47. Ten-no S.: *Chem. Phys. Lett.* **2000**, *330*, 169.
48. Klopper W. in: *Encyclopedia of Computational Chemistry* (P. v. R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III and P. R. Schreiner, Eds), Vol. 4, p. 2351. Wiley, Chichester 1998.
49. Klopper W., Samson C. C. M.: *J. Chem. Phys.* **2002**, *116*, 6397.
50. Noga J., Valiron P., Kedžuch S.: *J. Chem. Phys.*, to be submitted.
51. Partridge H.: *J. Chem. Phys.* **1989**, *90*, 1043.
52. Müller H., Kutzelnigg W., Noga J.: *Mol. Phys.* **1997**, *92*, 535.
53. Dunning T. H.: *J. Chem. Phys.* **1989**, *90*, 1007.
54. Wilson A. K., van Mourik T., Dunning T. H.: *J. Mol. Struct. (THEOCHEM)* **1996**, *388*, 339.
55. Gdanitz R.: *J. Chem. Phys.* **1998**, *109*, 9795.
56. Gdanitz R.: *J. Chem. Phys.* **1999**, *110*, 706.
57. Franke R., Müller H., Noga J.: *J. Chem. Phys.* **2001**, *114*, 7746.
58. Klopper W.: *Mol. Phys.* **2001**, *99*, 481.
59. Noga J., Valiron P., Klopper W.: *J. Chem. Phys.* **2001**, *115*, 2022.
60. Raffanetti R. C.: *J. Chem. Phys.* **1973**, *59*, 5936.
61. Schmidt M. V., Ruedenberg K.: *J. Chem. Phys.* **1979**, *71*, 3951.
62. Widmark P.-O., Persson B. J., Roos B.: *Theor. Chim. Acta* **1991**, *79*, 419.
63. Kedžuch S., Noga J., Valiron P.: *J. Comput. Chem.*, to be submitted.
64. Bak K. L., Jørgensen P., Olsen J., Klopper W.: *J. Chem. Phys.* **2000**, *112*, 9229.
65. Valiron P., Kedžuch S., Noga J.: *Chem. Phys. Lett.* **2003**, *367*, 723.