PHYSICAL REVIEW A VOLUME 25, NUMBER 1 JANUARY 1982

Implications and improvements of single-center expansions in molecules

Herbert H. Kranz and E. Otto Steinborn*
Institut für Theoretische und Physikalische Chemie, Universität Regensburg,
D-8400 Regensburg, West Germany

(Received 10 August 1981)

We first discuss convergence problems of single-center expansions of molecular wave functions in terms of exponential-type orbitals (ETO's). In a test calculation of H_2^+ we find that the expansion coefficients diverge quite rapidly when nonorthogonal basis functions are used. This behavior can cause serious numerical instabilities when the wave function is used in a configuration-interaction calculation. This problem does not occur when the ETO's are orthogonal. We then obtain an energy of -1.1022 a.u. (exact: -1.1026 a.u.) for H_2^+. Secondly, we present a contraction scheme that incorporates the information about the positions of the nuclei of the molecule similar to the information included in the LCAO scheme. It is therefore very efficient in reducing the dimension of the energy eigenvalue problem.

I. INTRODUCTION

There seems to be a common feature of quantum chemical calculations: With a few intuitively chosen assumptions and relatively moderate effort, one often gets surprisingly good results. The trouble, however, starts immediately when one tries to improve these results. A typical example is molecular *ab initio* calculations in which the molecular wave function is formed from a linear combination of atomic orbitals (LCAO).[1] The great advantage of this method is, of course, that the positions of the nuclei are automatically built into the trial wave function. In addition, the LCAO-MO's form good approximations to the true wave function in the vicinity of the nuclei when exponential-type atomic orbitals (ETO's) like Slater-type orbitals (STO's) are used. However, since these functions do not supply sufficient electron density in the bonding region between the nuclei, usually polarization functions with higher angular momentum quantum numbers have to be added. Hence complicated multicenter integrals have to be calculated. If Gaussian-type orbitals (GTO's) are used, instead, the computation of these integrals is much simpler. However, many more GTO's are usually required to achieve the desired accuracy because of the well-known deficiencies of these functions.

A quite different approach is the single-center expansion (SCE) (Ref. 1) of the molecular wave function. In this method the constituent basis functions are all centered at the same point, usually the center of gravity of the molecule. The basic idea is that any wave function can be expanded in terms of a complete set of basis functions centered at an arbitrary point in space. The major advantage of this method is that no complicated multicenter integrals occur. The price one has to pay is that many basis functions have to be included in order to obtain reasonable accuracy. Hence, the tenor of the earlier authors was usually pessimistic about the feasibility of this method.[2,3] Recently there has been renewed interest in this method[4] that has encouraged us to take a closer look at the problems associated with this method.

The aim of this paper is twofold. The first aim is to study the convergence behavior of different expansions of molecular wave functions. The convergence behavior of the expansion coefficients becomes important when the wave function is used in a subsequent configuration-interaction (CI) calculation. We therefore have to push the limit of single-center expansions in terms of ETO's further than it has been done before. We can do this because in the context of calculating multicenter integrals over ETO's the computation of single-center integrals over ETO's with high quantum numbers are required anyway.[5]

We find it necessary to take a closer look at properties like completeness of sets of basis functions and convergence, or as we find in one case, divergence of the expansion coefficients of the molecular wave function. The increase of the dimension of the eigenvalue problem is not the only bottleneck in these calculations. Diverging expansion coefficients and approximate linear dependence of the basis functions can effectively limit the size of basis sets. We apply the single-center expansion to H_2^+ and obtain very good results, provided we include a sufficiently high number of basis functions.

The second aim is to present a contraction scheme that combines some advantages of the LCAO ansatz with those of the single-center expansion. It is a side product of the work on the shifting of ETO's.[6] In this scheme the positions of the nuclei enter as input parameters like those in the LCAO ansatz. Since this information is built into the constituent wave functions, fewer of these functions are needed for simulating the exact molecular wave function near the nuclei. Hence, the dimension of the eigenvalue problem in the Rayleigh-Ritz method is greatly reduced. In this paper we compare the results obtained with a 60-term uncontracted basis with those obtained with a 3-term contracted basis.

This contraction scheme can readily be adopted to any nuclear geometry. It should be especially useful in relativistic single-center calculations.[7] There the dimension of the eigenvalue problem increases faster with increasing size of the basis set because the spinor in the Dirac equation has four components.

II. DEFINITIONS AND CLASSIFICATION OF INTEGRALS

In this section we list the definitions of functions and give a classification of the integrals used. The numerical details, however, in particular, the analytical expression, that were programed for the test calculations on H_2^+, are given in the appendices. We consider the following three one-electron integrals: the two-center nuclear attraction integral

$$N(f_1,f_2,\vec{R})\equiv \int d\vec{r}\, f_1^*(\vec{r})\frac{1}{|\vec{r}-\vec{R}|}f_2(\vec{r})\ , \tag{1}$$

the one-center kinetic-energy integral

$$T(f_1,f_2)\equiv \int d\vec{r}\, f_1^*(\vec{r})(-\tfrac{1}{2}\Delta)f_2(\vec{r})\ , \tag{2}$$

and the one-center overlap integral

$$S(f_1,f_2)\equiv \int d\vec{r}\, f_1^*(\vec{r})f_2(\vec{r})\ . \tag{3}$$

As basis functions $f(\vec{r})$ in Eqs. (1)–(3) we consider two different sets of exponential-type orbitals (ETO's). The first set are the B functions[8]

$$B_{N,L}^{M}(\vec{r})\equiv[2^{N+L}(N+L)!]^{-1}r^{L}e^{-r}\hat{k}_{N-1/2}(r)Y_L^M(\Omega_{\vec{r}})\ . \tag{4}$$

In Eq. (4) $\hat{k}_{N-1/2}$ and Y_L^M are reduced Bessel functions and surface sphericals harmonics in the Condon-Shortley phase convention, respectively.[9] Owing to the surface spherical harmonics, the B functions are orthogonal with respect to the angular momentum quantum number L. However, they are not orthogonal with respect to the radial quantum number N. This nonorthogonality has important consequences for the analytical and numerical properties of molecular wave functions that are expanded in terms of such a basis as we shall see below.

In contrast, the Λ functions form a set of basis functions that is orthogonal with respect to the radial and angular momentum quantum numbers. They are defined by[6,10,11]

$$\Lambda_{N,L}^{M}(\vec{r})\equiv\mathcal{N}(N,L)L_{N-L-1}^{(2L+2)}(2r)e^{-r}(2r)^{L}Y_L^M(\Omega_{\vec{r}}) \tag{5}$$

In Eq. (5) $L_N^{(\alpha)}$ are the generalized Laguerre polynomials, and the normalization factor is given by

$$\mathcal{N}(N,L)\equiv 2^{3/2}[(N-L-1)!/(N+L+1)!]^{1/2}\ . \tag{6}$$

III. CONVERGENCE OF GROUND-STATE ENERGY AND WAVE FUNCTION

As long as one is satisfied with the accuracy obtained with a few basis functions that are usually chosen by physical intuition, there is no need for dealing with questions like completeness of a set of basis functions, or, existence of formal expansions. Since we want to go beyond this initial stage of calculations we first recall a few general properties of sets of basis functions and then show how they affect our numerical calculations.

A. General considerations

A standard problem of functional analysis is to approximate a *known* function $f\in L^2$ by a set of basis functions $\{\phi_n\}_{n=1}^{\infty}$, with $\phi_n\in L^2(\mathscr{R}^3)$. The coefficients C_n^N of the Nth approximation

$$f^N = \sum_{n=1}^{N} C_n^N \phi_n \tag{7}$$

of f is determined by minimizing the norm $||f-f^N||$ (least-squares fit). If the basis functions are orthogonal the expansion coefficients C_n^N do not depend on N and therefore do not change when additional basis functions are included. The basis set $\{\phi_n\}_{L=1}^{\infty}$ is called complete in L^2 if for any given ϵ one can find an N such that

$$||f-f^N|| < \epsilon \ . \tag{8}$$

A basis set is called overcomplete if one can leave out some elements and the rest is still complete. It should be noted that nonorthogonal complete basis sets of *infinite* length are usually overcomplete.[12]

One might be tempted to conclude that completeness would imply the existence of a formal expansion

$$f = \sum_{n=1}^{\infty} C_n \phi_n \tag{9}$$

by taking the limit $N \rightarrow \infty$ of Eq. (7). However, this hope is only fulfilled with certainty if the basis set $\{\phi_n\}_{n=1}^{\infty}$ is orthogonal. It has been known for a long time that for nonorthogonal basis functions a formal expansion [Eq. (9)] need not exist.[13] The coefficients in Eq. (7) might diverge in the limit $N \rightarrow \infty$. In this case, if one tries to increase the size of the basis set they are bound to cause numerical instabilities in calculations that make use of these coefficients. This point should give rise to some concern because frequently used SCE basis sets like Slater[14] functions, or for that matter all LCAO functions,[15] are nonorthogonal. Orthogonalization of the basis functions does not help because this procedure involves the diagonalization of the overlap matrix which becomes numerically unstable.[15]

In quantum chemical calculations the actual problem is not to approximate a *known* function but to determine an *unknown* function by means of a variational principle, usually the Rayleigh-Ritz variational principle. In this procedure the ground-state eigenfunctions are approximated by minimizing the expectation value of the energy of the system

$$E[\Phi_N] = \frac{\langle \Phi_N | H | \Phi_N \rangle}{\langle \Phi_N | \Phi_N \rangle} \ . \tag{10}$$

It is worthwhile to draw the attention to the fact that this variation is not performed over the whole space L^2 but only over the subspace of functions that can be differentiated once, i.e., the Sobolev space $W_2^{(1)}$.[16–18] Functions like the Yukawa potential $\exp(-r)/r$, which is square integrable, are therefore excluded. In addition, basis sets that are complete in L^2 need not be complete in $W_2^{(1)}$, and if a basis set is not complete in $W_2^{(1)}$ the variational procedure need not yield the correct energy. A somewhat artificial but nevertheless striking example is due to Klahn and Bingel.[17] There the 1*s* function is deleted from the set of Slater orbitals. The remaining functions are still complete in L^2 but not in $W_2^{(1)}$, and the energy that is determined via the Rayleigh-Ritz variational principle with this basis set indeed converges towards the wrong limit. Hence, the frequently used method of deleting a finite number of basis functions from an overcomplete set in order to prevent that the overlap matrix becomes singular should be used with due care. Even if the resulting basis set is still complete in L^2, the damage done by omitting a function might not be correctable via the variational principle no matter how many other functions are included. Also the problem of diverging coefficients is present in the variational calculation when nonorthogonal basis sets are used.

In contrast, many of these complications are not present when functions are expanded in terms of a complete orthonormal basis set (CONS) like Λ functions. As a rule of thumb we find that expansions in terms of a CONS tend to be numerically more stable. This observation seems ultimately to be linked to the fact that the expansion coefficients C_n of some function f fulfill the Parceval equality[13]

$$\sum_{n=1}^{\infty} |C_n|^2 = ||f|| \ , \tag{11}$$

and are therefore bounded. In the limit of increasing size of an orthonormal basis set the expansion coefficients obtained via the Rayleigh-Ritz method converge towards the ones obtained via least-squares fit due to the uniqueness of the formal expansion whenever it exists.

B. Single-center calculations of H_2^+

In our single-center calculations of H_2^+ we put the center of the expansions at the midpoint of the molecule and keep only basis functions with even angular momentum quantum numbers l. From the work of Katriel[19] and Ali and Meath[20] we conclude that we are justified in doing so as long as the distance between the nuclei does not exceed 3

TABLE I. Comparison of the expansion coefficients of the wave function of $H_2{}^+$ in terms of B functions and Λ functions $L_{\max}=2$, $N_{\max}=16$, and $\alpha=2.7$.

		Coefficients of *B* functions			Coefficients of Λ functions				
L	N	$N_{\max}=6$	$N_{\max}=10$	$N_{\max}=16$	$N_{\max}=6$	$N_{\max}=10$	$N_{\max}=16$	L	N
0	1	0.318×10^{-1}	0.519×10^{-2}	0.174×10^{-1}	0.658×10^{0}	0.658×10^{0}	0.648×10^{0}	0	1
0	3	0.655×10^{1}	0.145×10^{2}	0.110×10^{3}	0.341×10^{0}	0.341×10^{0}	0.341×10^{0}	0	3
0	6	-0.829×10^{1}	-0.130×10^{4}	-0.175×10^{6}	-0.196×10^{-1}	-0.228×10^{-1}	-0.228×10^{-1}	0	6
0	9		0.735×10^{3}	0.682×10^{7}		0.356×10^{-4}	0.589×10^{-3}	0	9
0	12			-0.153×10^{8}			0.640×10^{-3}	0	12
0	15			0.127×10^{7}			-0.736×10^{-4}	0	15
0	16			-0.156×10^{6}			-0.651×10^{-3}	0	16
2	1	0.640×10^{-1}	0.321×10^{0}	0.378×10^{0}	0.179×10^{0}	0.179×10^{0}	0.179×10^{0}	2	3
2	3	-0.417×10^{1}	0.230×10^{2}	0.505×10^{2}	-0.249×10^{-2}	-0.227×10^{-2}	-0.228×10^{-2}	2	5
2	6	0.252×10^{1}	0.615×10^{3}	0.205×10^{6}	0.563×10^{-2}	-0.476×10^{-4}	-0.390×10^{-4}	2	8
2	9			-0.779×10^{7}		0.250×10^{-2}	0.186×10^{-2}	2	11
2	12			0.160×10^{8}			-0.755×10^{-3}	2	14
2	15			-0.123×10^{7}			-0.829×10^{-3}	2	17
2	16			0.148×10^{6}			0.976×10^{-3}	2	18

a.u. For larger distances, however, one should check the wave functions for spurious symmetry braking solutions by allowing the expansion center to float.[19,20] In this publication all calculations were performed at an internuclear distance $R=2.0$ a.u.

As basis functions we use the nonorthogonal set of B functions and the orthonormal set of Λ functions. The Λ functions have been applied to $H_2{}^+$ before.[2] However, not enough functions had been included for discussing the convergence of the ground-state energy, and the convergence of the expansion coefficients of the wave functions was not discussed.

From Table I we see that as we increase the size of the set of B functions the previously calculated coefficients do not converge to some finite value. This fact leads to rather large coefficients not only for some unrealistically large basis sets but already for the relatively moderately sized set of the first 16 radial wave functions per angular momentum quantum number. In contrast, when we approximate the ground-state wave function of $H_2{}^+$ by the orthonormal set of Λ functions the coefficients converge to some finite value. We also want to point out that our calculation with B functions broke down before reaching spectroscopic accuracy because of a numerical instability connected with the inversion of the overlap matrix. In contrast, there was no problem in reaching this accuracy with Λ functions.

Stewart[21] has calculated the energy limits that

TABLE II. Convergence of the ground-state energy of $H_2{}^+$ in single-center expansion in terms of Λ functions. The l limits are from Ref. 21.

$L_{\max}$ \ $N_{\max}$	6	10	16	20	25	l limit (Ref. 21)
0	−1.018 307	−1.018 482	−1.018 498	−1.018 499	−1.018 500	−1.018 503
2	−1.083 033	−1.083 478	−1.083 618	−1.083 649	−1.083 662	−1.083 681
4	−1.094 990	−1.095 940	−1.096 270	−1.096 348	−1.096 379	−1.096 438
6	−1.097 864	−1.099 096	−1.099 670	−1.099 792	−1.099 853	−1.099 967
8	−1.098 152	−1.100 004	−1.100 797	−1.100 990		1.101 264
10	−1.098 159	−1.100 083	−1.101 171	−1.101 470		1.101 825
12	−1.098 159	−1.100 084	−1.101 205	−1.101 574		−1.102 112
14	−1.098 159	−1.100 084	−1.101 206	−1.015 778		

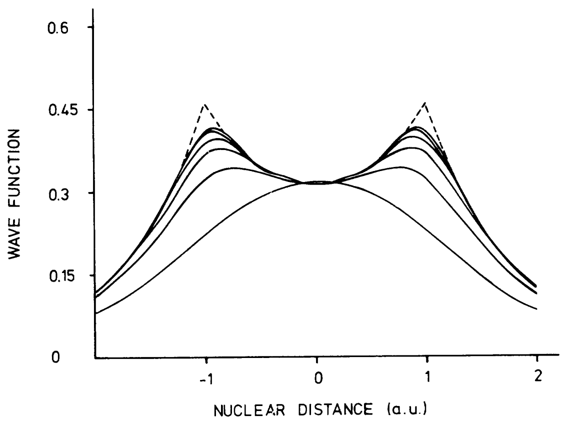

FIG. 1. Wave functions of $H_2{}^+$ along the molecular axis. Solid lines: single-center expansions in terms of Λ functions for $L_{\max}=0,2,4,6,8,10$. Λ functions with the first $N_{\max}=20$ radial quantum numbers to each L are included in the basis. Dashed line: exact wave function from Ref. 22.

can be obtained with functions centered at the midpoint of the molecular axis of $H_2{}^+$ when functions up to a given angular momentum L (≤ 12) are included. He calculated these limits by numerical integration of the pertinent radial differential equation. We come rather close to these limits with the first $N=25$ radial wave functions per angular momentum quantum number even without optimizing the scaling parameter α (Table II). When we optimize α ($\alpha \approx 6$) we find with $L=14$ and $N=20$ a ground-state energy of -1.1022 a.u. (exact: -1.1026 a.u.).[22]

In Fig. 1 we plot the wave functions along the molecular axis. We find good agreement in the bonding region and at large distances. Our approximation fails to reproduce the cusps of the exact wave function, a deficiency it shares with all finite single-center expansions.

A closer look at the coefficients in Table III shows that they change as additional basis functions are included. We recall that the coefficients determined via a least-squares fit procedure do not change when the size of an orthonormal basis set is increased (apart from the trivial change when the wave function is normalized to one in each order of approximation). The coefficients shown in Table III, however, indicate that the "direction" of the projection of the wave function onto the subspace of the smaller basis still changes once we include additional basis functions. This change occurs because we determine these coefficients via the Rayleigh-Ritz variational principle which corresponds to an approximation with respect to the norm of the Sobolev space $W_2^{(1)}$ and not of the Hilbert space L^2. It is only in the limit of the complete basis set that the Rayleigh-Ritz method and the least-squares fit procedure yield the same coefficients due to the uniqueness of formal expansions.

TABLE III. Convergence of the expansion coefficients of the ground-state wave functions of $H_2{}^+$ for the basis functions $\Lambda_{1,1}^{0}$ and $\Lambda_{3,2}^{0}$.

$L_{\max}$ \ $N_{\max}$	6	10	16	20	25
0	0.659 036	0.658 416	0.658 419	0.658 419	0.658 420
2	0.658 311	0.658 161	0.658 186	0.658 193	0.658 195
4	0.658 687	0.658 702	0.658 750	0.658 760	0.658 766
6	0.658 866	0.658 960	0.659 042	0.659 055	0.659 066
8	0.658 871	0.659 035	0.659 159	0.659 178	
10	0.658 761	0.659 039	0.659 195	0.659 233	
12	0.658 871	0.659 039	0.659 197	0.659 242	
14	0.658 871	0.659 039	0.659 197	0.659 242	
2	−0.178 692	−0.178 861	−0.178 944	−0.178 962	−0.178 971
4	−0.188 520	−0.189 015	−0.189 219	−0.189 269	−0.189 288
6	−0.190 639	−0.191 308	−0.191 669	−0.191 749	−0.191 786
8	−0.190 856	−0.191 951	−0.192 447	−0.192 575	
10	−0.190 862	−0.192 008	−0.192 705	−0.192 900	
12	−0.190 862	−0.192 009	−0.192 729	−0.192 971	
14	−0.190 862	−0.192 009	−0.192 730	−0.192 974	

IV. ATOMIC ORBITAL-TYPE CONTRACTION

A notorious drawback of the single-center expansion method is that usually large basis sets are required to yield acceptable accuracy. One source of this problem is the fact that the positions of the nuclei have to be incorporated in the trial function via the Rayleigh-Ritz variational principle which slows down the convergence of calculations.

In contrast, in the LCAO method this information is contained in the constituent atomic orbitals. Hence, fewer basis functions are needed to achieve surprisingly good results, especially when ETO's like STO's are used. However, it is usually difficult to improve these results because the AO's represent the molecular orbitals in the bonding region only poorly and it becomes increasingly difficult to calculate the required multicenter integrals for higher quantum numbers.

The central idea of our contraction scheme is to expand the very same wave functions one would use in an LCAO ansatz in terms of wave functions that are all centered at the same point, e.g., the center of the molecule. We use the shifting formula for Λ functions

$$\Lambda^{M}_{N,L}(\vec{r}-\vec{R})=\sum_{l_1 l_2}\sum_{m_1}\langle LM\,|\,l_1m_1\,|\,l_2m_2\rangle \times\sum_{n_1n_2} T^{n_2l_2;NL}_{n_1l_1}\Lambda^{m_1}_{n_1l_1}(\vec{r})\Lambda^{m_2}_{n_2l_2}(\vec{R})\ , \tag{12}$$

which was derived in Ref. 6. Useful features of Eq. (12) are the following: (a) the T coefficients are numerical constants that are independent of the geometry of the molecule and can be calculated once and for all, and (b) there is no division of the space as, e.g., in the Laplace expansion of the Coulomb operator. Therefore, Eq. (12) can be readily applied not only to Λ functions but also to integrals over Λ functions. In this way we have to calculate only integrals over functions that are all centered at the same point which brings about the simplifications of the SCE method.

On the other hand, if one starts with a given set of single-center basis functions, this scheme can be viewed as a prescription for contracting these basis functions. In this way the information about the positions of the nuclei is already incorporated in the trial wave function. If one finds it necessary to add to these AO-type functions a few functions that are centered at this central point, one need not calculate any additional integrals. In the LCAO scheme these functions would be called "floating functions." Clearly, this scheme can readily be transferred from one system to another, once the positions of the nuclei are specified. The eigenvalue problem one is left with is a generalized one because the functions of the contracted basis are no longer orthogonal. The dimension of this eigenvalue problem, however, is drastically reduced.

In our test calculations we compare the ground-state energy and wave functions along the principle axis of $H_2{}^+$. In the uncontracted basis we include the Λ functions up to the angular momentum $L=6$ and the first 15 radial quantum numbers to each L. Since only wave functions with even L contribute, this basis contains 60 functions. The contracted bases contain one (truncated) 1*s* function on each atom, which is expanded in terms of these 60 functions at the center, plus 1*s*, 1*s* +2*s*, or 1*s* +2*s* +3*s* Λ functions at the center. (We adapt the spectroscopic notation for Λ functions because no confusion is possible.) It is not surprising that the energies (Fig. 2) and wave function are rather sensitive to the choice of the scaling parameter α in the small contracted basis set. The Horowitz and Finkelstein LCAO basis set of $H_2{}^+$ (Ref. 23) also shows such a strong dependence of the ground state on the scaling parameter. The larger the basis set is the less sensitive the results are to a variation of α because the Λ functions form a complete set for any $\alpha>0$. We note in Fig. 3 and Table IV that the three basis functions consisting of a (truncated) 1*s* function at the atoms and a 1*s*

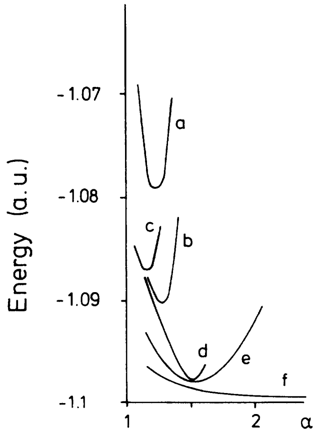

FIG. 2. Dependence of the ground-state energy of $H_2{}^+$ on the scaling parameter α for different basis sets. For curves a to e, contracted bases are used as indicated in the last column of Table IV. Curve f belongs to the uncontracted basis with $L_{\max}=6$ and $N_{\max}=15$.

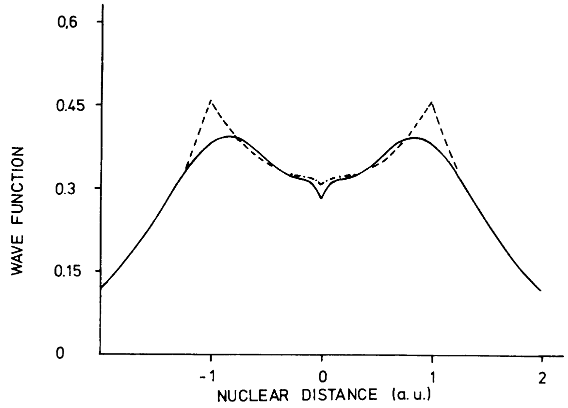

FIG. 3. Wave function of H_2^+ with contracted basis of curve d in Fig. 2 for $\alpha=1.5$ (solid line) and uncontracted basis with $L_{\max}=6$ and $N_{\max}=15$ (dash-dotted line). The dashed line is the exact wave (dashed-dotted line). The dashed line is the exact wave function from Ref. 22.

and a 2s function at the center yields results that are rather close to those of the uncontracted basis of 60 functions. The spurious cusp at the center (Fig. 3) comes from the 1s function. The variational principle has difficulties to suppress it because the contributions of this region to the integrals are reduced by the vanishing volume element at the origin. In the uncontracted basis, however, the cusp disappears within graphical accuracy when α is optimized. In Fig. 3 the wave functions with the contracted and uncontracted bases agree within graphical accuracy in the vicinity of the nuclei.

V. SUMMARY

In this paper we first have discussed some convergence problems in single-center expansions of molecular wave functions that could occur when the number of basis functions increases. When the basis functions are not orthogonal one has to be prepared that the expansion coefficients will diverge when the basis set is enlarged. This divergence can cause a numerical instability in a subsequent CI calculation with these coefficients and can effectively limit the size of the basis set. In our test calculation of H_2^+ with B functions we find that the coefficients diverge quite rapidly. A second source of a numerical instability lies in the generalized eigenvalue problem. With an increasing size of the basis set the basis functions become more and more linearly dependent and therefore the overlap matrix no longer can be inverted. Similar behavior should be expected when other nonorthogonal basis functions like Gaussian-type orbitals and ultimately LCAO are used.

In contrast, the expansion coefficients converge to a finite value when the basis functions are orthogonal. Using Λ functions as a basis set we came rather close to the limits that can be reached in single-center expansions for H_2^+ with functions up to a given angular momentum quantum number as calculated by Stewart.[21] We also have discussed the shape of the wave function of H_2^+ along the molecular axis.

Secondly, we have introduced a contraction scheme for single-center expansions in terms of Λ functions that incorporates the positions of the nuclei like the LCAO ansatz. Since the information about the positions of the nuclei no longer has to be determined via the Rayleigh-Ritz variational principle, this scheme is very efficient in reducing the dimension of the energy eigenvalue problem. It can be readily applied to molecular calculations because the positions of the nuclei are needed only as input parameters.

TABLE IV. Ground-state energy of H_2^+ for different contracted bases. The entry with * is from Ref. 23. The letters in the last column refer to the curves in Fig. 2.

α_{opt}	Basis functions on nuclei	in center	Energy (a.u.)	α dependence in Fig. 2
1.23	1s (truncated)		−1.0796	a
1.23	1s*		−1.0856	
1.28	1s (truncated)	1s	−1.0902	b
1.18	1s (truncated)	2s	−1.0897	c
1.52	1s (truncated)	1s + 2s	−1.0975	d
1.55	1s (truncated)	1s + 2s + 3s	−1.0980	e

APPENDIX A: INTEGRALS OVER *B* FUNCTIONS

We first turn to the nuclear attraction integral

$$N_{N_1N_2}^{L_1L_1}(\alpha,\vec{\mathrm{R}})=\int d\vec{\mathrm{r}}\,B_{N_1L_1}^{M_1}(\alpha\vec{\mathrm{r}})\frac{1}{|\vec{\mathrm{r}}-\vec{\mathrm{R}}|}B_{N_2L_2}^{M_2}(\alpha\vec{\mathrm{r}})\ . \tag{A1}$$

We proceed by expanding the product of *B* functions in Eq. (A1) in a *finite* sum of *B* functions with the argument doubled. After doing a little bit of algebra we obtain sums of integrals that consist of the Coulomb operator and one *B* function. These integrals are the basic nuclear attraction integrals of Ref. 24:

$$A_{N,L}^{M}(\vec{\mathrm{R}})=4\pi\alpha^{-2}\Big[(2L-1)!!\mathscr{Z}_L^M(\alpha\vec{\mathrm{R}})-\sum_{q=0}^{N+L}B_{q-L,L}^{M}(\alpha\vec{\mathrm{R}})\Big]\ . \tag{A2}$$

$\mathscr{Z}$ is the irregular solid spherical harmonic

$$\mathscr{Z}_Z^M(\vec{\mathrm{r}})\equiv r^{-L-1}Y_L^M(\Omega)\ . \tag{A3}$$

Our final result is

$$\begin{aligned}
N_{N_1N_2}^{L_1L_2}(\alpha,\vec{\mathrm{R}})={}&\pi\alpha^2[2^{2N_1+2N_2+L_1+L_2-2}(N_1+L_1)!(N_2+L_2)!]^{-1}\\
&\times\sum_l\langle l,m\,|L_1M_1|\,L_2M_2\rangle Y_l^m(\Omega)\sum_{s=0}^{N_1+N_2-2}(-1)^s2^{2s+1}\sum_{q=s}^{\min(N_1+N_2-2,2s+1)}\frac{(q+1)!}{(-2)^q(q-s)!(2s-q+1)!}\\
&\times\sum_{p=\max(0,q-N_1+1)}^{\min(q,N_2-1)}\frac{(2N_1-q+p-2)!(2N_2-p-2)!}{(q-p)!p!(N_1-q+p-1)!(N_2-p-1)!}\\
&\times\Bigg[(2\alpha R)^{-l-1}2^{-(L_1+L_2+2)}\frac{(\sigma+s+1)![2(\sigma+1)]!}{(l+1/2)(\sigma+1)!}\\
&\quad-\sum_{t=0}\binom{\Delta l}{t}\left[-\Delta l-\frac{2s+1}{2}\right]_t(L_1+L_2-t+s+1)!\\
&\quad\times(2\alpha R)^l\sum_{\mu=0}^{L_1+L_2-t+s+1}\frac{1}{2^\mu\mu!}\hat{k}_{\mu-l-1/2}(2\alpha R)\Bigg]\ ,
\end{aligned} \tag{A4}$$

with

$$\sigma\equiv(L_1+L_2+l)/2,\quad \Delta l\equiv(L_1+L_2-l)/2\ ,$$

the Pochhammer symbol $(a)_t$, and the Gaunt coefficient

$$\langle lm\,|L_1M_1|\,L_2M_2\rangle\equiv\int d\Omega\,Y_l^{m*}(\Omega)Y_{L_1}^{M_1}(\Omega)Y_{L_2}^{M_2}(\Omega)\ . \tag{A5}$$

The single-center overlap *S* and kinetic energy *T* integrals have been calculated in Ref. 24:

$$S_{N_1N_2}^{L_1}(\alpha)=\alpha^{-3}\frac{(2L_1+1)!!(2N_1+2N_2+2L_1-1)!!}{(2N_1+2N_2+4L_1+2)!!}\delta_{L_1,L_2}\delta_{M_1,M_2}\ , \tag{A6}$$

$$T_{N_1N_2}^{L_1L_2}(\alpha)=-(\alpha^2/2)[S_{N_1N_2}^{L_1L_2}(\alpha)-S_{N_1,N_2-1}^{L_1L_2}(\alpha)]\ . \tag{A7}$$

APPENDIX B: INTEGRALS OVER Λ FUNCTIONS

It turns out that the three-dimensional sums in Eq. (A4) slow down the computation of the nuclear attraction integrals. We, therefore, have used a different method for calculating the nuclear attraction integrals over Λ functions. First, we calculate these integrals for the lowest radial quantum number $N_1=L_1+1$.

The rest of the integrals we obtain by means of a 5-term recursion relation that is numerically stable up to about $N_1=L_1+25$ and $L_1\leq 12$, which should be sufficient for most applications.

For $N_1=L_1+1$ the nuclear attraction integrals reduce to

$$N^{L_1L_2}_{N_1=L_1+1,N_2}=\mathcal{N}(L_1+1,L_1)\mathcal{N}(N_2,L_2)\int d\vec{r}\,|\vec{r}-\vec{R}|^{-1}(2r)^{L_1+L_2}L^{(2L_2+2)}_{N_2-L_2-1}(2r)Y^{M_1^*}_{L_1}(\Omega)Y^{M_2}_{L_2}(\Omega)e^{-2r}\,. \tag{B1}$$

We use the Laplace expansion of the Coulomb operator which allows us to perform the angular part of the integration without any problem. For doing the radial part of the integrals the goal is to shift the indices of the Laguerre polynomials in such a way that one obtains a finite sum of integrals of the form

$$\int_{2R}^{\infty} dr\, L^{(\alpha)}_N(r)e^{-r} \tag{B2}$$

and

$$\int_0^{2R} dr\, r^{\alpha}L^{(\alpha)}_N(r)e^{-r} \tag{B3}$$

that are known analytically.[25] The result of these manipulations is

$$\begin{aligned}N^{L_1L_2}_{N_1=L_1+1,N_2}(\vec{R})=&\mathcal{N}(L_1+1,L_1)\mathcal{N}(N_2,L_2)e^{-2R}\\ &\times\sum_l\langle lm\,|L_1M_1|L_2M_2\rangle\frac{\pi}{2l+1}\\ &\times Y^m_l(\Omega)\left[(2R)^{L_1+L_2+2}\sum_{\nu=0}^{N_2-L_2-2}\frac{(L_2-L_1-l)_\nu}{\nu!(N_2-L_2-1-\nu)}L^{(L_1+L_2+l+3)}_{N_2-L_2-2-\nu}(2R)\right.\\ &+\frac{(L_2-L_1-l)_{N_2-L_2-1}}{(N_2-L_2-1)!}e^{-2R}(2R)^{-1}\gamma(L_1+L_2+l+3,2R)\\ &-(2R)^l(L_1+L_2-l+1)!\sum_{\nu=0}^{N_2+L_1-l}\left[\begin{matrix}N_2+L_2+1\\ \nu\end{matrix}\right]\left[\begin{matrix}N_2+L_1-l-\nu\\ L_1+L_2-l+1-\nu\end{matrix}\right](-1)^\nu\\ &\left.\times L^{(L_2-L_1+l)}_{N_2+L_1-l-\nu}(2R)\right],\end{aligned} \tag{B4}$$

where $\gamma(a,x)$ is the incomplete γ function.

In contrast to Eq. (A4), Eq. (B4) contains only two-dimensional sums of moderate lengths because the ν sums are limited by the binomial coefficients and the Pochhammer symbols.

The next step is to derive a recursion relation for the integrals with higher radial quantum numbers N_1. Such recursion relation can readily be found with the recursion relation for the Laguerre polynomial $L^{(\alpha)}_n$ that shifts the lower index n but leaves the upper index α unchanged.[25] The factor r that appears in this process is absorbed in Λ_{N_2,L_2}. After a short series of manipulation one finds

$$\begin{aligned}N^{L_1L_2}_{N_1N_2}(\vec{R})=&\left[\frac{1}{(N_1-L_1-1)(N_1+L_1+1)}\right]^{1/2}2(N_1-N_2-1)N^{L_1L_2}_{N_1-1,N_2}(\vec{R})\\ &+\left[\frac{(N_2-L_2-1)(N_2+L_2+1)}{(N_1-L_1-1)(N_1+L_1+1)}\right]^{1/2}N^{L_1L_2}_{N_1-1,N_2}(\vec{R})\\ &+\left[\frac{(N_2+L_2+1)(N_2-L_2)}{(N_1-L_1-1)(N_1+L_1+1)}\right]^{1/2}N^{L_1L_2}_{N_1-1,N_2+1}(\vec{R})\\ &-\left[\frac{(N_1-L_1-2)(N_1+L_1)}{(N_1-L_1-1)(N_1+L_1+1)}\right]^{1/2}N^{L_1L_2}_{N_1-2,N_2}(\vec{R})\,.\end{aligned} \tag{B5}$$

The recursion relation [Eq. (B5)] connects five integrals with the same angular momentum quantum number L_1 and L_2 and adjacent radial quantum number N_1 and N_2. The price one has to pay for avoiding the array of three-dimensional sums in Eq. (A4) is that one has to calculate almost twice as many integrals $N^{L_1 L_2}_{L_1+1,N_2}$, i.e., instead of calculating the integrals $N^{L_1 L_2}_{L_1+1,N_2}$ up to some $N_2 = L_2 + N_{\max}$, one has to calculate them up to $N_2 = L_2 + 2\times N_{\max} - 1$. Nevertheless, the method based on Eqs. (B4) and (B5) for calculating the nuclear attraction integrals is faster than the method based on Eq. (A4), provided one calculates a whole array of integrals up to some set of maximal quantum numbers. The kinetic energy integral has been given by Hagstrom and Shull [see Eq. (7) of Ref. 3]:

$$T^{L',L}_{N',N} = \frac{(2N_< + 1)(2L+1)!}{(2L+3)2^L} \frac{\mathcal{N}(N_>,L)}{\mathcal{N}(N_<,L)} \delta_{L,L'} \tag{B6}$$

for $N \neq N'$, and

$$T^{L,L'}_{N,N} = -\frac{1}{2}\left[1 - \frac{(2N+1)(2L+1)!}{(2L+3)!!2^{L-1}}\right]\delta_{L,L'} \tag{B7}$$

for $N = N'$.

ACKNOWLEDGMENTS

We wish to thank Dr. E. Filter and Mr. E. J. Weniger for helpful discussions. Dr. H. P. Trivedi has kindly provided the *T* coefficients. The Gaunt coefficients and spherical harmonics were computed with programs supplied by Mr. Weniger. Financial support through a grant by Deutsche Forschungsgemeinschaft is gratefully acknowledged. Computing time and facilities were provided by Rechenzentrum der Universität Regensburg.

---

*Author to whom correspondence should be addressed.

[1] A. C. Hurley, *Introduction to the Electron Theory of Small Molecules* (Academic, London, 1976).

[2] K. M. Howell and H. Shull, J. Chem. Phys. 30, 627 (1959).

[3] S. Hagstrom and H. Shull, J. Chem. Phys. 30, 1314 (1959).

[4] J. Ladik and J. Cizek, J. Chem. Phys. 73, 2357 (1980).

[5] H. P. Trivedi and E. O. Steinborn (unpublished).

[6] E. Filter and E. O. Steinborn, J. Math. Phys. 21, 2725 (1980).

[7] For a recent review of relativistic calculations see J. P. Desclaux, Phys. Scr. 21, 436 (1980).

[8] E. Filter and E. O. Steinborn, J. Math. Phys. 19, 79 (1978).

[9] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge Univeristy Press, Cambridge, 1935).

[10] E. A. Hylleraas, Z. Phys. 54, 347 (1929).

[11] P. O. Löwdin and H. Shull, Phys. Rev. 101, 1730 (1956).

[12] B. Klahn and W. A. Bingel, Int. J. Quantum Chem. 11, 943 (1977).

[13] R. Courant and D. Hilbert, *Methoden der mathematischen Physik I* (Springer, Berlin, 1968), p. 44.

[14] L. L. Combs and C. P. Miller, Int. J. Quantum Chem. 10, 455 (1976).

[15] P. -O. Löwdin, in *Advances in Quantum Chemistry*, edited by P. -O. Löwdin (Academic, New York, 1970), Vol. 5, p. 185.

[16] S. L. Sobolev, *Applications of Functional Analysis in Mathematical Physics* (American Mathematical Society, Providence, 1963).

[17] B. Klahn and W. A. Bingel, Theor. Chim. Acta (Berlin) 44, 9 (1977).

[18] B. Klahn and W. B. Bingel, Theor. Chim. Acta (Berlin) 44, 27 (1977).

[19] J. Katriel, Int. J. Quantum Chem. 6, 541 (1972).

[20] M. K. Ali and W. J. Meath, Int. J. Quantum Chem. 6, 949 (1972).

[21] R. F. Stewart, Mol. Phys. 24, 879 (1972).

[22] D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. R. Soc. London 246, 215 (1953).

[23] B. N. Finkelstein and G. E. Horowitz, Z. Phys. 48, 118, 448 (1929).

[24] E. Filter and E. O. Steinborn, Phys. Rev. A 18, 1 (1978).

[25] M. Magnus, F. Oberhettinger, and R. P. Soni, *Formulas and Theorems for the Special Functions of Mathematical Physics* (Springer, Heidelberg, 1966), Sec. 5.5.