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Configuration interaction calculations with terms linear in the interelectronic coordinate for the ground state of H_3^+. A benchmark study

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The CISD-$R12$ method is applied to the ground states of H_2 and H_3^+ at their equilibrium configurations, with both bare nuclear Hamiltonian (BNH) and self-consistent field (SCF) references with eight basis sets that range from 10 s (i.e., ten contracted s-type Gaussians) to $30s20p12d9f$. With the largest basis set, the energy of H_2 is obtained with an error of $2\mu E_h$, while for H_3^+, the error is probably smaller and the best calculated energy of $-1.343\,835 E_h$ is supposed to be accurate to all indicated figures. The BNH reference is always superior to the SCF reference. The relativistic corrections are evaluated at the SCF level by means of "direct perturbation theory" both for H_2 and H_3^+. The Hylleraas-SCF methods and related concepts for the construction of an optimum reference function are discussed in the Appendix.

I. INTRODUCTION

The ion H_3^+ is the simplest polyatomic molecule consisting of three nuclei and two electrons and is hence—as suggested a few years ago[1]—a possible benchmark molecule for computational chemistry in the 90s. Accurate calculations of H_3^+ are, in fact, much more difficult than, e.g., for H_2.

In this paper, we are concerned with the energy of the ground state of H_3^+ at its (equilateral triangular) equilibrium geometry, i.e., with the lowest eigenvalue of the nonrelativistic Born–Oppenheimer (or rather clamped nuclei) Hamiltonian at this geometry. A rather complete bibliography on this particular problem has recently been given,[2] such that we need not repeat it. In a forthcoming paper, we shall deal with the potential energy surface and properties related to it, such as the fundamental vibrational frequencies.

While the ground state energy of H_2 has been calculated to six significant figures almost 30 years ago[3] and is now known to ten figure accuracy,[4] the situation is much different for H_3^+, where up to about 1970 only two figure accuracy ($1.3\cdots E_h$), up to about 1980 not more than three-figure accuracy ($-1.34\cdots E_h$), and up to about 1990 four-figure accuracy ($-1.343\cdots E_h$) was achievable. Only very recently the fifth figure became stable ($-1.3438\cdots E_h$), provided one used either method with sophisticated inclusion of electron correlation, or Green's function Monte Carlo methods. The best strictly variational result is $-1.343\,827\,9 E_h$,[5] but only the first five figures are definite. The so far best "traditional" quantum chemical approach of configuration interaction (CI) type[6] led to $-1.343\,40\cdots E_h$, although one must admit that this study was not meant just for the equilibrium geometry, but for the entire potential surface, for which it did very well, while some more accurate calculations[2,7] were limited to the equilibrium nuclear configuration.

We have decided to apply our CISD-$R12$ method[8,9] to the H_3^+ problem using a systematic hierarchy of basis sets. To test the accuracy that is achievable, we have first performed similar calculations for H_2.

The method is outlined in Sec. II, and technical details on the program and on the basis sets are described in Sec. III. The results for H_2 are discussed in Sec. IV and those for H_3^+ in Sec. V. In addition to energies, we have also calculated properties. This is, e.g., not possible (or has not been done) with the Green's function Monte Carlo method.[2] We have further included relativistic corrections to the ground state energy of H_3^+ (this only at the SCF level).

Our method is not variational, i.e., it does not satisfy an upper bound property, but it converges much faster to the exact energy than most conventional variational calculations.

The main message of this paper is that for both H_2 and H_3^+ the CISD-$R12$ calculations converge sufficiently well that the final error is only of the order of at most 2–3 μhartree. The approach based on the bare nuclear Hamiltonian reference is always superior to that with SCF reference. We further conclude that a $10s8p6d$ basis is sufficiently close to saturation and can hence be used for highly accurate calculations of the potential hypersurface.

II. METHOD

The method is essentially that described in Ref. 8. The ansatz for the wave function is

$$\Psi=(1+\tfrac{1}{2}r_{12})\Phi+\chi, \tag{2.1}$$

$$\chi=\sum_{\mu} c_\mu \varphi_\mu, \tag{2.2}$$

where Φ is a single Slater determinant reference function, either the two-electron eigenfunction of the bare nuclear Hamiltonian (without electron interaction), referred to as BNH, or the SCF wave function.

The function χ that accounts for the electron correlation not taken care of by the r_{12} term is expanded in products φ_μ of basis functions as in ordinary CI with single and

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double substitutions. Since there is only a single term linear in r_{12}, it is obvious that the reference function to be multiplied by r_{12} should be chosen carefully. In a previous study of He-like atoms,[8] it was found that the BNH reference is usually very good and much better than the SCF reference. The optimum reference corresponds to a slight shielding of the BNH, but this concept is not easily generalized to the molecular case. In the Appendix on Hylleraas SCF, we say a few words on the optimum reference.

We have to deal with the following matrix elements:

$$D=\langle\Phi|(1+\tfrac{1}{2}r_{12})^2|\Phi\rangle, \tag{2.3}$$

$$S_{0\mu}=\langle\Phi|1+\tfrac{1}{2}r_{12}|\varphi_\mu\rangle/\sqrt{D}, \tag{2.4}$$

$$S_{\mu\nu}=\langle\varphi_\mu|\varphi_\nu\rangle, \quad \text{for } \mu\neq 0,\ \nu\neq 0, \tag{2.5}$$

$$H_{00}=\langle\Phi|(1+\tfrac{1}{2}r_{12})H(1+\tfrac{1}{2}r_{12})|\Phi\rangle/D, \tag{2.6}$$

$$H_{0\mu}=\langle\Phi|(1+\tfrac{1}{2}r_{12})H|\varphi_\mu\rangle/\sqrt{D}, \tag{2.7}$$

$$H_{\mu\nu}=\langle\varphi_\mu|H|\varphi_\nu\rangle, \quad \text{for } \mu\neq 0,\ \nu\neq 0. \tag{2.8}$$

We assume all functions and matrix elements to be real.

An essential ingredient of the CISD-$R$12 method is the assumption that the unperturbed problem (BNH or SCF) is solved exactly, i.e., that the basis is saturated at the one-electron level for the required symmetry species. This has, of course, to be checked. This assumption allows us to rewrite the matrix elements (2.6) and (2.7). Let us do this first for the BNH case for which

$$H_0\Phi=(T+V)\Phi=E_0\Phi. \tag{2.9}$$

It is convenient to introduce the operator U_{12} (Ref. 8)

$$\begin{aligned} U_{12}&=\frac{1}{2}[T,r_{12}]+\frac{1}{r_{12}}\\ &=-\frac{1}{2}\frac{\mathbf{r}_1-\mathbf{r}_2}{r_{12}}(\nabla_1-\nabla_2), \quad T=T(1)+T(2). \end{aligned} \tag{2.10}$$

It has the properties

$$\langle\Phi|U_{12}|\Phi\rangle=\left\langle\Phi\left|\frac{1}{r_{12}}\right|\Phi\right\rangle, \tag{2.11}$$

$$\langle\Phi|\tfrac{1}{2}r_{12}U_{12}|\Phi\rangle=\tfrac{3}{4} \tag{2.12}$$

for arbitrary Φ. Moreover, there is the general operator identity

$$\tfrac{1}{2}[r_{12},[H_0,r_{12}]=[r_{12},U_{12}]=1, \tag{2.13}$$

which allows us to rewrite Eq. (2.6) as

$$H_{00}=\left\langle\Phi\left|\left(1+\frac{1}{2}r_{12}\right)^2\left(H_0+\frac{1}{r_{12}}\right)+\frac{1}{4}\right|\Phi\right\rangle\Big/D, \tag{2.14}$$

or assuming the validity of Eq. (2.9) as

$$H_{00}=E_0+\left(\frac{5}{4}+\left\langle\Phi\left|\frac{1}{r_{12}}\right|\Phi\right\rangle+\frac{1}{4}\langle\Phi|r_{12}|\Phi\rangle\right)\Big/D. \tag{2.15}$$

For Eq. (2.7), we get

$$\begin{aligned} H_{0\mu}=H_{\mu 0}&=\left\langle\varphi_\mu\left|\left(1+\frac{1}{2}r_{12}\right)\left(H_0+\frac{1}{r_{12}}\right)\right|\Phi\right\rangle\Big/\sqrt{D}\\ &\quad+\left\langle\varphi_\mu\left|\left[T,\frac{1}{2}r_{12}\right]\right|\Phi\right\rangle\Big/\sqrt{D}\\ &=E_0S_{0\mu}+\left\langle\varphi_\mu\left|\frac{1}{2}+U_{12}\right|\Phi\right\rangle\Big/\sqrt{D}. \end{aligned} \tag{2.16}$$

If Φ is a Hartree–Fock wave function, it satisfies

$$F\Phi=[F(1)+F(2)]\Phi=2\epsilon\Phi \tag{2.17}$$

instead of Eq. (2.9).

$$F(1)=T(1)+V(1)+2J(1)-K(1), \tag{2.18}$$

where $J(1)$ and $K(1)$ are the Coulomb and exchange Coulomb operators, respectively.

Then Eqs. (2.14) and (2.15) are replaced by

$$\begin{aligned} H_{00}&=\left\langle\Phi\left|\left(1+\frac{1}{2}r_{12}\right)^2\left(F+\frac{1}{r_{12}}-2J+K+\frac{1}{4}\right)\right|\Phi\right\rangle\Big/D\\ &=2\epsilon+\left[\frac{5}{4}+\left\langle\Phi\left|\frac{1}{r_{12}}\right|\Phi\right\rangle+\frac{1}{4}\langle\Phi|r_{12}|\Phi\rangle\right.\\ &\quad\left.-\left\langle\Phi\left|\left(1+\frac{1}{2}r_{12}\right)^2(2J-K)\right|\Phi\right\rangle\right]\Big/D. \end{aligned} \tag{2.19}$$

The evaluation of Eq. (2.19) is somewhat more difficult than that of Eq. (2.16) due to the contribution

$$\langle\Phi|r_{12}(2J-K)|\Phi\rangle, \tag{2.20}$$

the exact evaluation of which would lead to three-electron integrals involving r_{12} and r_{13}^{-1}.[10] We approximate this in the spirit of our standard approximation[10] by means of a completeness insertion. The validity of this completeness insertion only requires that the basis is saturated at the one-electron level. In the atomic case, it is even sufficient that the basis is saturated up to a given finite l value.

Our CISD-$R$12 just described is, of course, a special case of Hylleraas CI. One important advantage over conventional Hylleraas CI is that matrix elements such as

$$\left\langle\varphi_\mu\left|\frac{Z}{r_1}r_{12}\right|\varphi_\nu\right\rangle, \tag{2.21}$$

which require numerical integration,[11] and which make Hylleraas CI slow even for two-electron systems, are not needed here.

The price that we pay is that we lose the upper bound property, but we gain from the fact that we can use a much larger one-electron basis than in conventional Hylleraas CI, such that at the end, we achieve a higher accuracy.

The difference between our CISD-$R$12 for BNH reference and conventional Hylleraas CI, limited to the ansatz (2.1), is easily seen. In Hylleraas CI, one would evaluate the matrix elements (2.6) and (2.7) without making the assumption (2.9). One would usually not make the transformations to Eqs. (2.15) and (2.16), but Eq. (2.14) and the first line of Eq. (2.16) would still be valid.

The "errors" of our matrix elements with respect to rigorously calculated ones are hence

$$\Delta H_{00}=\langle\Phi|(1+\tfrac{1}{2}r_{12})^2(H_0-E_0)|\Phi\rangle/D, \qquad (2.22)$$

$$\Delta H_{\mu 0}=\langle\varphi_\mu|(1+\tfrac{1}{2}r_{12})(H_0-E_0)|\Phi\rangle\sqrt{D}. \qquad (2.23)$$

The errors can be made arbitrarily small by choosing the orbital basis close to complete at one-electron level. Although a definite proof is not available, there is evidence[12] that the convergence at the one-electron level is exponential with the number of angular moments included (unlike at the two-electron level, where it only goes as an inverse-power law). In the atomic case, the basis need only be saturated up to a fixed l value.

Of course, one may decide to evaluate these errors explicitly, but this would require matrix elements of type (2.21), the evaluation of which is very slow,[11] and which represent the bottleneck of Hylleraas-CI calculations of two-electron systems.

The same conclusions are also reached for CISD-$R12$ with Hartree–Fock reference. The error of our CISD-$R12$ energy (i.e., its difference to the exact eigenvalue of the Born–Oppenheimer Hamiltonian) consists of three parts of which the first two are positive (i.e., consistent with the variation principle), while the third one is unbounded. These are (L is always the highest l value included in the basis):

(1) the fact that the correlation cusp condition is not satisfied exactly leads to an error contribution $\sim(L+1)^{-3}$ with a very small coefficient[8];

(2) the basis incompleteness at the two-electron level implies an error of $\sim(L+1)^{-7}$;

(3) the fact that the one-electron problem is not solved exactly is supposed to cause an error exponential in L, as is the completeness insertion for the SCF reference.

Taking these three errors together, one has to conclude that for sufficiently large L, the third error will always be negligible with respect to the other two, such that eventually an upper bound property holds.

In the case of He-like ions, the BNH eigenfunction is a very good choice, while the optimum choice[8] corresponds to the eigenfunctions of a slightly screened BNH with

$$Z^*=Z-0.304/Z+0.14/Z^2. \qquad (2.24)$$

The screening which minimizes the one-configuration energy

$$Z_{\text{eff}}=Z-\tfrac{5}{16} \qquad (2.25)$$

leads to much poorer results. In Ref. 8, a tentative explanation of the unexpected excellent performance of the BNH reference has been given. A corollary of this is that for this choice, the formal partial wave expansion of H_{00} practically coincides with that of the exact energy.[13]

We have investigated the possibility to choose Φ such that it minimizes the expectation value H_{00}. We refer to this as the Hylleraas SCF.[14] Details are found in the Appendix.

For the present study (see Secs. IV and V), a better reference than BNH is not needed.

It should be mentioned that the option between different reference configurations only exists for genuine two-electron systems. For atoms or molecules with more than two electrons, it is almost compulsory to stay in the framework of Møller–Plesset (MP) perturbation theory or coupled cluster (CC) theory with a SCF (or MCSCF) reference. In fact, in our MP-$R12$ (Ref. 9) and CC-$R12$ (Ref. 15), we have used the SCF reference, accepting that one loses somewhat with respect to optimum convergence.

In our work on systems with more than two electrons, two "standard approximations" "A" and "B" have been introduced.[10] Either of them implied the assumption that the unperturbed problem is solved exactly and, in addition, some completeness insertions at the many-electron level were assumed to hold {which imply truncation errors—in the atomic case—of $O[(L+1)^{-5}]$ for approximation A and $O[(L+1)^{-7}]$ for approximation B}. For two-electron systems, there is no need to introduce such completeness relations (only for SCF reference at the one-electron level) and we are automatically at least at the level of standard approximation B.

Let us finally mention that another simplification of the matrix elements (2.6) and (2.7) alternatively to Eqs. (2.15) and (2.16) is possible. Let us choose φ_μ such that they are eigenfunctions of H_0 with eigenvalue ϵ_μ,

$$H_0\varphi_\mu=\epsilon_\mu\varphi_\mu. \qquad (2.26)$$

This is formally possible by taking φ_μ as a product of one-electron functions that diagonalize $H_0(1)$ or $F(1)$ in the given basis, but it relies on assuming that the BNH or HF problem is solved exactly for all eigenvalues and not just for the lowest one. This is much more restrictive than the assumption that Eq. (2.9) is solved exactly. Anyhow, assuming Eq. (2.26), one can simplify Eq. (2.7) to

$$H_{0\mu}\approx\epsilon_\mu\langle\Phi|(1+\tfrac{1}{2}r_{12})|\varphi_\mu\rangle/\sqrt{D}=\epsilon_\mu S_{0\mu}, \qquad (2.27)$$

which is evaluated more easily than Eq. (2.16), mainly since the matrix elements of the U_{12} operator are not needed.

There is no change for H_{00}.

One should expect that the simplification characterized by Eq. (2.26) is much poorer than that characterized by Eq. (2.16). We have performed some numerical tests with this simplification (see Sec. VI), which confirmed this expectation on the whole, although the results are not as bad as one might have thought.

III. COMPUTER PROGRAMS AND BASIS SETS

The TURBOMOLE[16] suite of programs was used for SCF (and BNH) calculations. The two-electron integrals needed by the CISD-$R12$ approach were calculated by a modified[17] version of the HERMIT[18] integral generator. The transformation of atomic orbital (AO) integrals into the orthogonal basis was done by the SORE[19] program. The aforementioned programs rest on direct integral evaluation techniques. It is noteworthy that without such techniques, the benchmarks of the present work would have been prohibited by disk space limitations.

The computations were carried out on the IBM RS/6000 workstations (models 550 and 320 H) of the

TABLE I. Contraction coefficients.

	H_2		H_3^+	
	BNH	SCF	BNH	SCF
s	0.026 535	0.026 523	0.026 709	0.026 637
	0.007 224	0.007 071	0.008 165	0.007 695
	0.114 186	0.114 442	0.113 001	0.113 649
	0.216 107	0.214 512	0.226 022	0.221 104
	0.706 792	0.708 238	0.697 443	0.702 032
s	0.090 375	0.090 843	0.091 733	0.091 618
	0.254 801	0.257 504	0.246 378	0.251 387
	0.700 611	0.697 626	0.707 733	0.702 966
p	0.070 528	0.071 856	0.069 553	0.071 762
	0.183 818	0.213 737	0.113 401	0.142 383
	0.804 313	0.776 182	0.867 915	0.841 826
d	0.027 242	0.027 959	0.034 690	0.040 595
	0.010 217	0.013 219	0.043 363	0.010 525
	0.982 552	0.979 981	0.953 981	0.977 284
f	0.016 667	0.025 081	0.011 480	0.015 910
	0.476 660	0.535 151	0.200 902	0.303 741
	0.601 102	0.538 617	0.846 657	0.759 353

Lehrstuhl für Theoretische Chemie at Bochum and on the Cray Y-MP/8-32 of the Forschungszentrum Jülich (KFA).

We have used two basis sets of Gaussian-type orbitals (GTOs). The first one is a contracted $10s8p6d4f$ set constructed from a $16s10p8d6f$ primitive set. Two diffuse *s*-type functions were added to the $14s$ even-tempered GTO basis set of Schmidt and Ruedenberg[20] by straightforward extrapolation. If these exponents are numbered 1–16 from highest to lowest, then the numbers 6–15 are used for the *p* set, the numbers 7–14 are used for the *d* set, and the *f*-type set consists of the functions 8–13. This primitive set has been contracted as $(5,3,8\times1)s$, $(3,7\times1)p$, $(3,5\times1)d$, and $(3,3\times1)f$, where four different sets of contraction coefficients have been used. The contraction coefficients are the coefficients of the doubly occupied BNH or SCF orbital for H_2 ($R=1.4a_0$) or H_3^+ (D_{3h}, $R=1.65a_0$), calculated with the full $16s10p8d6f$ set. Only pure spherical harmonic components of GTO basis sets were used in the present work. Then, the contraction coefficients for H_2 are uniquely defined, since the totally symmetric σ_g representation is contained only once in the representations spanned by the *s*, *p*, *d*, or *f* functions. However, in the case of H_3^+ in D_{3h} symmetry, the totally symmetric a_1' representation is contained twice in the reducible representation spanned by the *d* or *f* functions. Therefore, the contraction coefficients for these functions are chosen as a compromise between the coefficients of the two a_1' components. We give the contraction coefficients in Table I.

The second set is a fully uncontracted $30s20p12d9f$ basis corresponding to the $30s20p12d9f4g$ set used by Franke and Kutzelnigg (basis III of Ref. 21), but without *g* functions. The recommended BNH limits were calculated with the above $30s20p12d9f$ basis augmented with six *g* functions with *s* exponents 19–24.

Orthogonal sets were constructed by canonical orthogonalization.[22] Eigenvectors of the overlap matrix with eigenvalues less than 10^{-5} were eliminated throughout. Table II shows the number of eliminated functions in each irreducible representation. This number is the same for both BNH and SCF contractions.

IV. DISCUSSION OF THE RESULTS FOR H_2

In Table III, the results of conventional CISD calculations as well as CISD-$R12$ calculations both with BNH reference and SCF reference for the H_2 ground state at the distance of 1.4 bohr are collected.

TABLE II. The number of functions eliminated by canonical orthogonalization with the criterion $\epsilon_i(S)<10^{-5}$.

Basis set	Irreducible representation								
H_2 $D_{\infty h}$, $R=1.4a_0$	σ_g	σ_u	π_g	π_u	δ_g	δ_u	ϕ_g	ϕ_u	N^a
$10s$	0	0	⋯	⋯	⋯	⋯	⋯	⋯	20
$10s8p$	0	2	0	0	⋯	⋯	⋯	⋯	66
$10s8p6d$	0	4	0	0	0	0	⋯	⋯	124
$10s8p6d4f$	1	4	0	2	0	0	0	0	175
$30s$	0	0	⋯	⋯	⋯	⋯	⋯	⋯	60
$30s20p$	0	4	0	0	⋯	⋯	⋯	⋯	176
$30s20p12d$	0	7	0	1	0	0	⋯	⋯	291
$30s20p12d9f$	2	8	0	2	0	0	0	0	412
H_3^+ D_{3h}, $R=1.65a_0$	a_1'	a_2'	e'	a_1'	a_2''	e''			N^a
$10s$	0	⋯	0	⋯	⋯	⋯			30
$10s8p$	0	0	2	⋯	0	0			98
$10s8p6d$	0	2	3	0	0	0			184
$10s8p6d4f$	0	3	5	1	0	1			260
$30s$	0	⋯	1	⋯	⋯	⋯			90
$30s20p$	0	1	4	⋯	0	0			261
$30s20p12d$	0	3	6	0	0	0			435
$30s20p12d9f$	2	5	8	0	0	1			614

[a] The number of remaining orthonormal basis functions.

TABLE III. Ground state energy of the H_2 molecule at $R=1.4a_0$. Energies are in $-E_h$. Results are obtained with contracted ($10s8p6d4f$) and uncontracted ($30s20p12d9f$) basis sets.

Basis set	CISD[a]	BNH reference CISD-$R$12	SCF reference CISD-$R$12
$10s$	1.154 875	1.174 718	1.173 138
$10s8p$	1.172 271	1.174 392	1.174 357
$10s8p6d$	1.173 955	1.174 469	1.174 454
$10s8p6d4f$	1.174 223	1.174 474	1.174 467
$30s$	1.154 891	1.174 716	1.173 132
$30s20p$	1.172 293	1.174 393	1.174 359
$30s20p12d$	1.173 985	1.174 470	1.174 456
$30s20p12d9f$	1.174 285	1.174 474	1.174 469

[a] In case of contraction, the coefficients are taken from the BNH calculation with the $10s8p6d4f$ basis set.

While the conventional CI results converge slowly with an increase of the basis size, being in error of 0.2 mhartree for the largest basis, the CISD-$R$12 results converge much faster. For the BNH reference, both for the basis sets ($10s8p6d4f$) and ($30s20p12d9f$), there is only a difference of ~ 2 μhartree with respect to the exact result. For the SCF reference, the convergence is somewhat poorer, and for the largest basis, the error is $\sim 7 \mu E_h$.

One also reads from Table III—comparing the ($10s\cdots$) with the ($30s\cdots$) basis set—that saturation within one l value ($s,p,d,\ldots$) is practically achieved with the ($10s\cdots$) sets for the CISD-$R$12 calculations, but not at all for the ordinary CISD calculations.

Reference values from the literature are found on Table IV.

To reduce the error to less than $1 \mu E_h$, one probably has to include g functions or functions with higher l in the basis. A better alternative is possibly to care for an optimum reference (see the Appendix).

We have pointed out in Sec. II that our method is not strictly variational, i.e., it is not guaranteed that the exact energy is approached from above. However, we have also mentioned that it is relatively easy to satisfy the assumption (2.9) to any desired accuracy. One sees, in fact, from Table V that the reference-state energy E_0 is only in error by a few μE_h provided that the basis is sufficiently saturated up to d AOs. This means that for sufficiently large basis sets, the deviations from an upper bound property are negligible and one does approach the exact energy from above. This is confirmed by the values in Table III. Only for the BNH reference with basis sets limited to s functions one overshoots the exact energy, though only by $\sim 0.3 mE_h$.

Further inspection of Table V reveals that E_0 converges somewhat faster for the SCF reference. This is not unexpected. The BNH reference corresponds to the H_2^+ ground state, in which induction (polarization) effects are large. To take care of the polarization of the wave function at one nucleus by the other nucleus, basis functions with

TABLE IV. A comparison of the best results of the present work with reliable *ab initio* calculations. Geometries are the same as in Table II (if not indicated otherwise). Energies are in $-E_h$.

		Method/basis set	Energy	Literature
H_2				
	E_{BNH}	$30s20p12d9f$ GTO	1.854 252 4	This work
		$30s20p12d9f6g$ GTO	1.854 252 7	This work
			1.854 252 7	Wind (Ref. 31)
	E_{SCF}	$30s20p12d9f$ GTO	1.133 629 5	This work
		Finite element method	1.133 629 572	Yang *et al.* (Ref. 32)
		Finite difference method	1.133 629 573	Sundholm (Ref. 33)
	E_{total}	CISD-$R$12/$30s20p12d9f$ GTO	1.174 474 4	This work
		Explicitly correlated functions	1.174 475 668	Kolos *et al.* (Ref. 4)
		Hylleraas-CI/$15s7p2d1f$	1.174 474 67[a]	Frye *et al.* (Ref. 34)
		Gaussian geminals	1.174 474 85[a]	Alexander *et al.* (Ref. 35)
		Variational Monte Carlo	1.174 453(26)	Alexander *et al.* (Ref. 7)
H_3^+				
	E_{BNH}	$30s20p12d9f$	2.041 902 2	This work
		$30s20p12d9f6g$ GTO	2.041 902 9	This work
	E_{SCF}	$30s20p12d9f$ GTO	1.300 371 7	This work
		$13s5p3d$ GTO	1.300 365	Frye *et al.* (Ref. 5)
		$30s20p12d9f$ GTO	1.300 399 8[b]	This work
		Coordinate space numerical HF	1.300 40[b]	Becke and Dickson (Ref. 36)
		Momentum space numerical HF	1.300 41(4)[b]	Alexander *et al.* (Ref. 37)
	E_{total}	CISD-$R$12/$30s20p12d9f$ GTO	1.343 835 1	This work
		Green's function Monte Carlo	1.343 835(1)	Anderson (Ref. 2)
		Hylleraas-CI/$13s5p3d$ GTO	1.343 827 9	Frye *et al.* (Ref. 5)
		Gaussian geminals	1.343 822 0	Alexander *et al.* (Ref. 35)
		Gaussian geminals	1.343 814	Wenzel (Ref. 38)
		Variational Monte Carlo	1.343 819(66)	Alexander *et al.* (Ref. 7)

[a] Calculated at $R=1.4011a_0$.

[b] Calculated at $R=1.6405a_0$.

TABLE V. Reference state energy E_0[a] and expectation value H_{00}[b] calculated with BNH and SCF wave functions of the H_2 molecule at $R=1.4a_0$. Energies are in $-E_h$. Results are obtained with contracted ($10s8p6d4f$) and uncontracted ($30s20p12d9f$) basis sets.

	BNH reference		SCF reference	
Basis set	E_0	H_{00}	E_0	H_{00}
$10s$	1.834 957	1.167 633	1.128 538	1.139 498
$10s8p$	1.854 045	1.165 292	1.133 570	1.138 173
$10s8p6d$	1.854 249	1.165 313	1.133 628	1.138 203
$10s8p6d4f$	1.854 252	1.165 314	1.133 629	1.138 204
$30s$	1.834 961	1.167 633	1.128 542	1.139 490
$30s20p$	1.854 050	1.165 292	1.133 572	1.138 174
$30s20p12d$	1.854 250	1.165 313	1.133 629	1.138 204
$30s20p12d9f$	1.854 252	1.165 314	1.133 629	1.138 204

[a]Expectation value of the BNH or SCF reference function Φ_0.
[b]Expectation value of $(1+\frac{1}{2}r_{12})\Phi_0$ [Eq. (2.6)].

TABLE VI. Ground state properties (in atomic units) of the H_2 molecule ($R=1.4a_0$ along the z axis). Results are obtained with the $10s8p6d4f$ basis sets.

				Literature	
	SCF[a]	CISD[b]	CISD-$R12$[c]	Monte Carlo[d]	Other theory[e]
p_x^2	0.8376	0.8693	0.8694	0.870(1)	
p_z^2	0.5769	0.6109	0.6110	0.611(1)	
r_{1A}	1.5554	1.5491	1.5488	1.548(2)	1.548 8
r_{1A}^2	3.0639	3.0377	3.0368	3.031(6)	3.036 4
$1/r_{1A}$	0.9081	0.9127	0.9128	0.910(2)	0.912 8
x^2	0.7769	0.7619	0.7617	0.764(2)	0.761 7
z^2	1.0202	1.0239	1.0235	1.017(2)	1.023 0
p^4	12.254	13.065	13.094	13.0(4)	13.249
$\delta(r_{1A})$	0.4450	0.4545	0.4551	0.459(1)	0.460 15

[a]The $10s8p6d4f$ basis set with SCF contraction.
[b]With BNH contraction.
[c]With BNH reference and contraction coefficients.
[d]Alexander *et al.* (Ref. 23).
[e]Kolos and Wolniewicz (Ref. 3).

large l are needed. In a SCF calculation of H_2, on the other hand, the other nucleus is essentially shielded and induction effects are much smaller. So for the SCF calculation of H_2, a smaller basis is sufficient than for H_2^+.

The "dominant" matrix element H_{00}, also documented in Table V, shows a similar convergence pattern as E_0. The superiority of the BNH reference is obviously somehow related to the fact that H_{00} for BNH is much closer to the exact ground state energy of H_2 than the H_{00} for SCF reference.

If we call $E\text{-}H_{00}$ the "residual correlation energy," then this is $10.2mE_h$ for BNH reference and $37.3mE_h$ for SCF reference. The corresponding value for the He atom ground state with BNH reference is $27.1mE_h$, and it is reduced for the optimum shielding reference (OS) to $15.0mE_h$. For He, the error of calculations including up to $l=7$ was[8] $2.3\mu E_h$ for BNH reference and $0.4\mu E_h$ for OS reference. The analogous errors for l truncated at $L=3$ were ~ 5 and $\sim 1\mu E_h$, respectively. So actually, the BNH reference is definitely better for H_2 than for He, and also the convergence in terms of l is faster for H_2. There is hence less need for an improved reference than in the case of He.

Calculated properties of H_2 are found in Tables VI and VII. The agreement with the best available values from the literature is usually quite good. However, the improvement of CISD-$R12$ with respect to conventional CISD, at least for the ($10s8p6d4f$) basis, is rather small. This is not too surprising since all these properties are related to one-electron operators that are not very sensitive to short-range correlation.

It should be mentioned that the one-particle properties in Table VI were not evaluated as expectation values, but from a one-particle density matrix constructed from the wave functions by means of a completeness insertion. Therefore the last word on the effect of the r_{12} term on properties has probably not yet been said.

The one-electron properties were actually calculated as matrix traces of products of operators and density matrix representations. In conventional CISD, this is equivalent to the expectation value of the operator from the wave function, but in CISD-$R12$, it is not. In the latter case, we first project the CISD-$R12$ wave function onto the space spanned by the conventional Slater determinants, normalize the projection, and then form a density matrix as usual.

With respect to factors of 2 (number of electrons) contained in the definitions of the one-electron operators, we adopt the notation of Ref. 23. Expectation values of two-electron operators such as r_{12}^{-1} or $\delta^3(r_{12})$ depend somewhat more on the r_{12} term.

The polarizabilities in Table VII have been evaluated by finite perturbation theory as second derivatives of the energy.

V. DISCUSSION OF THE RESULTS FOR H_3^+

The results for the energy of the H_3^+ ground state in its equilateral triangular configuration are collected in Table VIII.

TABLE VII. Static dipole polarizabilities in atomic units of the H_2 and H_3^+ molecules at their equilibrium geometries (as in Tables III and V), obtained with the $10s8p6d4f$ basis set. An electric field of 0.01 a.u. was applied as finite perturbation.

				Literature	
	SCF[a]	CISD[b]	CISD-$R12$[c]	Monte Carlo[d]	Other theory
H_2					
α_{xx}	4.615	4.584	4.583	4.4(2)	4.5786[e] 4.5074[f]
α_{zz}	6.455	6.397	6.393	6.3(2)	6.3866[e] 6.4454[f]
H_3^+					
α_{xx}	3.593	3.546	3.546	3.5(3)	3.5949[f]
α_{zz}	2.252	2.202	2.202	2.0(3)	2.2357[f]

[a]The $10s8p6d4f$ basis set with SCF contraction.
[b]With BNH contraction.
[c]With BNH reference and contraction coefficients.
[d]Alexander *et al.* (Ref. 23).
[e]Bishop and Cheung (Ref. 39).
[f]SCF results obtained by Augspurger and Dykstra (Ref. 40) calculated at $R=1.6504a_0$.

TABLE VIII. Ground state energy of the H_3^+ molecule at equilibrium geometry (D_{3h}, $R=1.65a_0$). Energies are in $-E_h$. Results obtained with contracted (10s8p6d4f) and uncontracted (30s20p12d9f) basis sets.

Basis set	CISD[a]	BNH reference CISD-$R$12	SCF reference CISD-$R$12
10s	1.311 812	1.334 382	1.333 993
10s8p	1.341 148	1.343 898	1.343 962
10s8p6d	1.343 287	1.343 834	1.343 823
10s8p6d4f	1.343 578	1.343 834	1.343 828
30s	1.311 981	1.334 632	1.334 401
30s20p	1.341 232	1.343 913	1.343 974
30s20p12d	1.343 338	1.343 835	1.343 825
30s20p12d9f	1.343 656	1.343 835	1.343 831

[a] The same as footnote a in Table III.

The convergence pattern is similar to that for H_2. Again with the largest basis, the conventional CISD is off by $\sim 0.2mE_h$. The contribution of f-type AOs is $0.3mE_h$ both for H_2 and H_3^+, while d-type AOs contribute $\sim 1.7mE_h$ in H_2 and $\sim 2.1mE_h$ in H_3^+. In CISD-$R$12 with BNH reference, the energy appears to be converged to $-1.343\,835E_h$, while with the best SCF reference we miss $\sim 4\mu E_h$.

The convergence of the reference state energy E_0 and the expectation value H_{00} are seen in Table IX. For H_3^+, E_0 converges somewhat more slowly than for H_2. The increment of f AOs for BNH is as much as $13\mu E_h$. However, as seen from Table IV, inclusion of g functions lowers this value by only $\sim 1\mu E_h$, such that it can be regarded as practically converged. The explanation of the slower convergence is of course that BNH corresponds to H_3^+, an H atom polarized by two protons. Hence there are much larger induction effects than in H_2.

Again, as for H_2, the SCF energy of H_3^+ converges faster than the BNH energy. The value of $-1.300\,372E_h$ can be regarded as stable. It may be compared with the best value of $-1.300\,365$ from the literature[5] (see Table IV) for this geometry, obtained with a significantly smaller basis, that is close to the value for our (10s8p6d) basis.

TABLE IX. Reference state energy E_0[a] and expectation value H_{00}[b] calculated with BNH and SCF wave functions of the H_3^+ molecule (D_{3h}, $R=1.65a_0$). Energies are in $-E_h$. Results obtained with contracted (10s8p6d4f) and uncontracted (30s20p12d9f) basis sets.

	BNH reference		SCF reference	
Basis set	E_0	H_{00}	E_0	H_{00}
10s	1.988 417	1.331 931	1.280 852	1.303 443
10s8p	2.040 846	1.340 759	1.300 151	1.307 786
10s8p6d	2.041 887	1.340 662	1.300 369	1.307 682
10s8p6d4f	2.041 902	1.340 659	1.300 371	1.307 681
30s	1.988 872	1.332 160	1.281 037	1.303 771
30s20p	2.040 937	1.340 778	1.300 174	1.307 797
30s20p12d	2.041 889	1.340 662	1.300 370	1.307 683
30s20p12d9f	2.041 902	1.340 659	1.300 372	1.307 682

[a] The same as footnote a in Table V.

[b] The same as footnote b in Table V.

The expectation value H_{00} converges faster than E_0, and we can regard the value of $-1.340\,659$ for BNH reference as converged. Again H_{00} for BNH is very close to the exact H_3^+ energy (residual correlation energy $\sim 3mE_h$), while for SCF reference, the residual correlation energy is $43mE_h$. The superiority of the BNH reference is even more pronounced than in the case of H_2. The trend from He to H_2 is continued.

To estimate the error of our best H_3^+ energy of $-1.343\,835$ in a reliable way is, of course, not easy. One can certainly not object that it should be of the same order of magnitude as for H_2, where it was $2\mu E_h$. There are indications that the error should be smaller for H_3^+. For the same number of electrons, the basis is larger for H_3^+. The much smaller residual correlation energy (i.e., the small importance of excited configurations) is another indication. Furthermore the stability of E on the addition of f functions to the basis is an indication that the error may be less than $1\mu E_h$.

The effect of f AOs is not seen from Table VIII because we have rounded off at the microhartree position. With more figures, we get for BNH reference

10s8p6d,	$-1.343\,833\,67$,
10s8p6d4f,	$-1.343\,834\,28$,
30s20p12d,	$-1.343\,834\,75$,
30s20p12d9f,	$-1.343\,835\,09$.

The f AOs lower the energy by $0.61\mu E_h$ for the first family of basis sets and by $0.34\mu E_h$ for the second family.

One should not overlook that the convergence to the exact energy of CISD-$R$12 with BNH reference for H_3^+ is from below up to the sets without f functions, while it appears to be from above for larger sets. For H_2, it was from above—excluding s-only basis sets. Again this is not too surprising. In fact, for the basis sets used here (except the largest one), the one-particle energy E_0 is not fully converged, and hence the deviations from the upper-bound property controlled by the validity of Eq. (2.9), dominate the error, while the corrections to the $(1+\frac{1}{2}r_{12})\Phi$ term are less important than in the case of H_2. This confirms our expectation that increments for $l>3$ should lower the energy such that the value with f AOs is actually an upper bound. This is consistent with the observation for the SCF reference, where the validity of the counterpart of Eq. (2.9) is reached earlier (essentially for the basis sets without f functions), such that the results for the largest basis sets appear to be practically upper bounds.

The best previous variational result is that of Frye *et al.*[5] (see Table IV), using a Hylleraas-CI method. This does obviously not represent the limit of what is achievable with Hylleraas CI, but rather what is feasible with present computer facilities.

If one argues that the basis of Frye *et al.* (13s5p3d) is not saturated, as is seen from the missing $7\mu E_h$ at the SCF level, while it is probably good enough for the correlation part, one might add the SCF error to the overall energy and get $-1.343\,835$, in agreement with our best result.

TABLE X. Ground state properties (in atomic units) of the H_3^+ molecule (equilateral triangle in the xy plane with $R=1.65a_0$). Results are obtained with the $10s8p6d4f$ basis sets.

				Literature	
	SCF[a]	CISD[b]	CISD-$R$12[c]	Monte Carlo[d]	Other theory[e]
p_x^2	0.7594	0.7942	0.7942	0.792(4)	
p_z^2	1.0650	1.0987	1.0989	1.104(6)	
r_{1A}	1.5755	1.5715	1.5714	1.572(8)	
r_{1A}^2	2.9850	2.9686	2.9680	2.97(2)	
$1/r_{1A}$	0.8522	0.8553	0.8553	0.856(5)	0.855 19
x^2	0.7631	0.7607	0.7605	0.760(4)	0.759 13
z^2	0.5514	0.5397	0.5396	0.541(4)	0.540 85
p^4	7.1780	7.6319	7.6532	7.7(1)	
$\delta(r_{1A})$	0.3518	0.3592	0.3597	0.363(2)	

[a] The $10s8p6d4f$ basis set with SCF contraction.
[b] With BNH contraction.
[c] With BNH reference and contraction coefficients.
[d] Alexander *et al.* (Ref. 23).
[e] Salmon and Poshusta (Ref. 41).

We are not dissatisfied that the same value has also been suggested recently by Anderson[2] on the basis of his Green's function Monte Carlo calculation, with an indicated statistical error of $1\mu E_h$. We have no feeling for the reliability of this error estimate, noting that there were a few earlier calculations by Anderson *et al.*, namely, $-1.344\pm0.013E_h$ from 1975,[24] $-1.3439\pm0.0002E_h$ from 1981,[25] $-1.343\,76\pm0.000\,03E_h$ from 1987,[26] and $-1.343\,87\pm0.000\,05$ from 1988,[27] such that the 1987 and 1988 estimates hardly overlapped and that that of 1987 does definitely not include the present best value.[2]

Some expectation values for H_3^+ are found on Table X. The reference values from the literature are probably less accurate than ours, such that these can be regarded as recommended values. Again the difference between the results from conventional CISD and CISD-$R$12 is very small.

VI. THE SIMPLIFIED APPROACH

In Table XI, we compare the results of the "standard" CISD-$R$12 method with those of the simplified version characterized by Eq. (2.27). For the ($10s8p6d4f$) basis, the simplified version does not look too bad, in particular, in connection with the SCF reference, but on the whole, the convergence pattern is less systematic and definitely inferior to the standard approach.

TABLE XI. A comparison of the original method [Eq. (2.16)] with an alternative method which avoids integrals of the type $[T,r_{12}]$, i.e., Eq. (2.27).

	BNH reference		SCF reference	
Basis set	Eq. (2.16)	Eq. (2.27)	Eq. (2.16)	Eq. (2.27)
H_2 $R=1.4a_0$				
$10s$	1.174 718	1.173 520	1.173 138	1.172 117
$10s8p$	1.174 392	1.174 469	1.174 357	1.174 414
$10s8p6d$	1.174 469	1.174 476	1.174 454	1.174 456
$10s8p6d4f$	1.174 474	1.174 480	1.174 467	1.174 468
H_3^+ D_{3h}, $R=1.65a_0$				
$10s$	1.334 381	1.333 266	1.333 993	1.333 147
$10s8p$	1.343 898	1.344 124	1.343 962	1.344 172
$10s8p6d$	1.343 834	1.343 853	1.343 823	1.343 832
$10s8p6d4f$	1.343 834	1.343 839	1.343 828	1.343 831

TABLE XII. First order relativistic direct perturbation theory (DPT) applied to H_2 ($R=1.4a_0$) and H_3^+ (D_{3h}, $R=1.65a_0$). Contributions to Eq. (7.1) as expectation values of the SCF determinant obtained with the contracted $10s8p6d4f$ basis sets. $E_{\rm rel}^{(2)}$ is in μE_h; all other entries are in atomic units.

	H_2	H_3^+
ϵ_0	$-0.594\,66$	$-1.207\,88$
$\langle\chi_0\vert\chi_0\rangle$	0.563 04	0.645 95
$\langle\chi_0\vert V\vert\chi_0\rangle$	$-0.959\,11$	$-1.476\,33$
$\langle\chi_0\vert J\vert\chi_0\rangle$	0.353 99	0.408 29
$E_{\rm rel}^{(2)}$[a]	-14.394	-15.326
Literature[b]	-14.399	

[a] $E_{\rm rel}^{(2)}=(1/c^2)E_2$ with $c=137.035\,989\,5$ a.u., as in Ref. 21.
[b] The Dirac–Fock result by Yang, Heinemann, and Kolb (Ref. 32).

The simplification with respect to our standard approach (where matrix elements of the operator U_{12} explicitly arise) is actually not so important that there is any reason to prefer the "simplified approach."

VII. RELATIVISTIC CORRECTION TO THE SCF ENERGY OF H_3^+

If one is able to calculate energies to microhartree accuracy, one also needs to worry about corrections that go beyond the nonrelativistic Born–Oppenheimer Hamiltonian. We have therefore decided to evaluate approximate relativistic corrections, by means of the direct perturbation theory,[21,28] that has turned out to be rather powerful—and numerically much better behaved than the use of the Breit–Pauli Hamiltonian. We have limited ourselves to the lowest order in c^{-1}, i.e., to $c^{-2}E_2$. Neglect of the Breit interaction and of correlation effects are additional approximations. One should later go beyond these two approximations, while the limitation to the leading term in c^{-1} is perfectly uncritical (the next term will be smaller by $\sim10^{-4}$).

Within the direct perturbation approach, the leading correction E_2 at the SCF level is obtained as

$$E_2=2\langle\chi_0|V+J-\epsilon_0|\chi_0\rangle,\quad \chi_0=\tfrac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{p}\varphi_0, \tag{7.1}$$

where φ_0 is the occupied Hartree–Fock spin orbital with energy ϵ_0, V is the nuclear attraction, and J is the Coulomb operator generated by φ_0.

The contributions that enter Eq. (7.1) and the final value for the relativistic correction are given in Table XII. These must not be confused with the contributions that arise from the Breit–Pauli Hamiltonian (velocity mass, Darwin, etc.).

VIII. COMPUTER TIMES

In Table XIII, we give central processing unit (CPU) times in minutes as obtained on an IBM RS/6000 model 320 H workstation. Some calculations were done on a model 550 workstation. These were almost twice as fast.

TABLE XIII. CPU times in minutes on an IBM RS/6000 model 320 H workstation.

Basis set	15 iterations[a]	Integral transformation[b]
H_2		
10*s*8*p*6*d*	60	80
10*s*8*p*6*d*4*f*	390	460
30*s*20*p*12*d*	940	1 280
30*s*20*p*12*d*9*f*	5 120	6 050
H_3^{+c}		
10*s*8*p*6*d*	105	160
10*s*8*p*6*d*4*f*	680	950
30*s*20*p*12*d*	2 360	2 690
30*s*20*p*12*d*9*f*	10 040	12 310

[a] Typical values for SCF or CISD(-$R$12) iterations performed with the TURBOMOLE (Ref. 16) suite of programs.

[b] Utilizing the SORE (Ref. 19) program.

[c] In D_{3h} symmetry.

SORE calculations on the Cray Y-MP/8-32 (KFA, Jülich) performed about ten times faster than those of Table XIII.

The SORE[19] program generates integrals of the type $(IP|JQ)$ over $1/r_{12}$, r_{12}, $[r_{12},T_1]$, and $[r_{12},T_2]$, where I and J are doubly occupied obitals, and where P and Q denote arbitrary orbitals. These integrals are evaluated only once and then stored. We see from Table XIII that evaluating these integrals in the orthogonal basis does not take more time than about 18 SCF iterations performed with the TURBOMOLE[16] program.

In a "direct-CI" approach for two-electron systems, a single CI iteration is essentially the same computation as one SCF iteration. Therefore, the CISD and CISD-$R$12 iterations were performed with the TURBOMOLE package, and the computer times are given in Table XIII.

All other computational work demands only negligible effort.

As an example, consider the H_3^+ ion with the 10*s*8*p*6*d*4*f* basis set. The total cost of one CISD-$R$12 calculation is 1630 minutes on a 320H workstation, consisting of one BNH calculation (negligible), one SORE integral transformation (950 min), and 15 CISD-$R$12 iterations (680 min) with TURBOMOLE. This means that such a calculation can be done easily within 24 h on a (designated) model 550 workstation. It is noteworthy that such a day's work is accurate to within a few (2–3) microhartrees.

We see from Table XIII that the calculations on H_3^+ take roughly twice as long as those on H_2. This holds as long as the D_{3h} symmetry of the equilateral triangular ion is fully exploited. Points on the potential energy surface with lower symmetry will, of course, take considerably longer.

IX. CONCLUSIONS

It has been possible to get a very accurate ground state energy of H_3^+ with the CISD-$R$12 method. There is strong evidence that the energy of $-1.343\ 835E_h$ is in error by at most 1 to $2\mu E_h$. Although our ansatz is more restricted than Hylleraas CI, the fact that no "expensive" integrals such as Eq. (2.21) are needed allows one to use very large basis sets and thus to beat the accuracy of the more flexible Hylleraas CI. Although the same accuracy has also been claimed for Green's functions Monte Carlo calculations, we doubt that these will be applicable to the accurate calculation of a full potential surface or to the evaluation of properties, which our method is.

We are in the somewhat fortunate situation that the convergence to the exact result is faster for H_3^+ than for H_2 and this is faster than for He-like ions. This means that in order to achieve microhartree accuracy for H_3^+, the BNH reference is perfectly alright. If one wants to push the accuracy still further, one has probably to care for an optimum single Slater determinant reference, or even to use a multiconfiguration reference.

The present results encourage us to be optimistic also with respect to CISD-$R$12 or CCSD-$R$12 calculations for molecules with more than two electrons.

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APPENDIX: HYLLERAAS SCF

A good reference function is essential for the fast convergence of the CISD-$R$12 method. It is therefore worthwhile to ask how one can find an optimum reference. One possibility is to minimize the expectation value H_{00} as defined by Eq. (2.6) with respect to the single Slater determinant Φ. We call this the Hylleraas SCF. In a "generalized Hylleraas SCF," one can replace the factor 1/2 in Eq. (2.6) by some arbitrary parameter γ and minimize with respect to γ as well. One can also minimize just with respect to γ for given Φ, but this is, of course, no longer the Hylleraas SCF. For the case of the He ground state, generalized Hylleraas-SCF calculations have been performed long ago[29,30] with the result

$$\gamma=0.35, \quad H_{00}=-2.898\ 06E_h, \tag{A1}$$

i.e., a "residual correlation energy" of $-5.7mE_h$, compared to $-27.1mE_h$ for BNH reference and $-15.0mE_h$ for optimum shielded reference as characterized by Eq. (2.24).

With a 10 s Huzinaga basis, we were able to reproduce the result (A1). It should also be mentioned that the result for $\gamma=0.5$ does not differ much from the optimum H_{00}; one namely gets $H_{00}=2.895\ 273E_h$ for $\gamma=0.5$.

For H_2 at $R=1.4a_0$, we have obtained the Hylleraas-SCF energy (using a $6s3p1d$ basis)[14]

$$\begin{aligned}&\gamma=0.5, \quad H_{00}=-1.171\,698,\\ &\gamma_{\text{opt}}=0.43, \quad H_{00}=-1.171\,970.\end{aligned} \tag{A2}$$

The residual correlation energy is $-2.5mE_h$ (for $\gamma=0.5$), while for BNH reference, it is $-9.2mE_h$. So the gain with respect to BNH is less spectacular than in the case of He and it will probably be even smaller for H_3^+.

Some tentative studies with the Hylleraas SCF as reference for CISD-$R12$ were not too encouraging (i.e., they did not appear to be really superior to BNH reference), but more careful studies are necessary.

The criterion for the best reference is probably not that one should minimize H_{00}. In fact, the Brillouin condition corresponding to the minimum of H_{00} is that

$$\langle\Phi|(1+\tfrac{1}{2}r_{12})H(1+\tfrac{1}{2}r_{12})|\Phi_i^a\rangle=0, \tag{A3}$$

where Φ_i^a is a singly excited configuration. What we need is, however, that matrix elements of the type (2.16) are as small as possible, in particular, that

$$\langle\Phi|(1+\tfrac{1}{2}r_{12})H|\Phi_i^a\rangle=0, \tag{A4}$$

$$\langle\Phi|U_{12}^\dagger-\lambda r_{12}|\Phi_i^a\rangle=0. \tag{A5}$$

A method where one determines Φ such that Eqs. (A4) and (A5) hold may be termed a "Hylleraas–Brillouin" method.

We can now return to the observation that the "best" reference Φ is obviously much closer to the BNH than the SCF wave functions. In other words, the reference Φ does not want to be shielded much. There are two partial explanations. One is illustrated for the He ground state.

A wave function

$$\Psi(1,2)=Ne^{-\alpha r_1-\alpha r_2}(1+\tfrac{1}{2}r_{12}) \tag{A6}$$

can for small r_{12} be written as

$$\Psi(1,2)\approx N\exp(-\alpha r_1-\alpha r_2+\tfrac{1}{2}r_{12}). \tag{A7}$$

If $\mathbf{r}_1$ and $\mathbf{r}_2$ are collinear and $r_2>r_1$, the effective nuclear charge for electron 2 is $\alpha-\frac{1}{2}$, i.e., r_{12} introduces automatically some shielding.

Another explanation starts from the condition (A5). The effective one-electron operator, of which the occupied molecular orbital (MO) is eigenfunction, is $H_0+\widetilde{J}$ with

$$\widetilde{J}(1)=\int(U_{12}^\dagger-\lambda r_{12})|\varphi(2)|^2d\tau_2. \tag{A8}$$

The operator $\widetilde{J}(1)$ which replaces the operator $J(1)$ of Hartree theory is much different from the latter. Especially there is no strong short-range repulsion.

In spite of their long experience, the authors are still somewhat suprised how well the ansatz (2.1) works. The factor $1+\frac{1}{2}r_{12}$ has been introduced to correct the behavior of the wave function for small r_{12}. However, this factor should be unphysical for large r_{12} and one might have thought that one ought to multiply r_{12} by a damping factor that falls off rapidly for large r_{12}. It turns out that the exponential decay of the wave function with r_1 and r_2 makes the situation extremely unlikely that r_{12} is large, at least for atoms.[8] In a diatomic molecule such as H_2, the "pair distribution function" has a local maximum (or shoulder) near $r_{12}=R$ (R being the internuclear distance). This local maximum is somewhat underestimated in the one-determinant approximations; it is enhanced by the $(1+\frac{1}{2}r_{12})$ factor, which is a desired feature, introducing some left–right correlation. This means that the need to use a two-configuration reference necessary for large R is somewhat reduced. A similar argument holds for H_3^+. This explains somehow why H_2 and H_3^+ take even more advantage from the r_{12} term than does He.

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