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Accurately solving the electronic Schrödinger equation of atoms and molecules using explicitly correlated $(r_{12}$-$)$ MR-CI: the ground state potential energy curve of N_2

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Abstract

The recently proposed MR-CI ansatz which contains terms linear in the interelectronic distances (r_{12}) is used to compute the potential energy curve of N_2 by means of r_{12}-MR-ACPF. The computed spectroscopic constants with the respective errors, e.g. ΔD_e $(-0.2$ kcal/mol$)$, ΔR_e $(+1 \times 10^{-4}$ Å$)$ and $\Delta \omega_e$ $(+2$ cm$^{-1})$, are found to be in excellent agreement with values derived from experimental spectra. With only a moderate computational effort, we reach accuracies which are probably out of reach of present day (traditional) CI-methods and computers. © 1998 Elsevier Science B.V.

1. Introduction

The most common approach to approximately solve the electronic Schrödinger equation for medium sized atoms or molecules is to expand the solution in antisymmetrized products of orbitals, i.e. Slater-determinants. However, since this traditional CI ansatz does not have the analytical properties of the exact wavefunction, one cannot expect fast convergence to the solution. It turns out that the region where two electrons of opposite spin approach each other closely (here the exact wavefunction is linear in the interelectronic distance r_{12}), becomes the bottleneck [1], limiting the truncation error $\Delta E(L) := E(L \to \infty) - E(L)$ of the computed energy $E(L)$, which arises when the basis set used is truncated at the angular momentum quantum number L, to $\Delta E(L) \propto L^{-3}$ (for details see for example Ref. [2]). Therefore to increase the accuracy of a CI calculation by a factor of 10, the value of L must be more than doubled! Furthermore, assuming that the number n of basis functions grows as $n \propto L^2$ and that the CPU time T needed to solve a particular set of CI-like equations grows as $T \propto n^4$, then one may roughly estimate the accuracy ΔE achieved by using a certain amount of CPU time with the relation

$$\Delta E \propto 1/\sqrt{T} \tag{1}$$

Including terms that are linear in r_{12} in the expansion of the wavefunction dramatically increases the efficiency in the case of two-electron atoms and molecules, but the straightforward extension to many electron systems leads to integrals over

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the coordinates of 3 and 4 electrons whose sheer number ($\propto n^8$) cancels the improvement in the convergence of the energy with respect to the number of basis functions, leaving the relation between accuracy and CPU time, Eq. (1), unaltered.

Kutzelnigg [1] carefully analyzed the problem and suggested that, in order to keep things simple enough to allow for the extension of Hylleraas' ansatz to many electron systems, one should append to the traditional CI expansion, only those terms linear in r_{12} that are constructed from orbitals which are occupied in the reference. Later a many electron theory was formulated [3], which is applicable to arbitrary closed-shell systems and where the evaluation of 3- and 4-electron integrals is entirely avoided by means of the approximate resolution of the identity (RI) and by summing certain contributions in closed form; the remaining contributions which could not be treated this way could be neglected because they only give rise to errors converging faster to zero than the truncation error of traditional CI (see above). Meanwhile, this so-called ''r_{12}-method'' has been implemented into methods as sophisticated as CC(SDT) (the triples being approximated) and has been applied to a variety of problems (see Ref. [4] for a review).

Recently [2,5] the present author has generalized the method of Kutzelnigg and coworkers to arbitrary open-shell and multiple-reference cases. In the present Letter, as the first application of r_{12}-MR-CI, we calculate the potential energy curve of nitrogen molecule (N_2) at chemical distances.

2. Theory

Since the theory has already been described in detail in Refs. [2,5], we will only give a broad outline here. In the following we use the notation of the cited papers and make use of the Einstein summation convention. It is further assumed that the basis set used is approximately complete up to a certain l-quantum number so that the RI-approximation can be applied (''standard approximation'' (SA) [3]).

We append to the CI expansion all those terms that can be generated from all the reference Slater determinants ϕ on which the former is based by applying the recipe

$$\phi_{ij}^{\boldsymbol{kl}} := \bar{R}_{\kappa\lambda}^{\boldsymbol{kl}} \hat{a}_{ij}^{\kappa\lambda} \phi = \left(\bar{r}_{\kappa\lambda}^{\boldsymbol{kl}} \hat{a}_{ij}^{\kappa\lambda} - \bar{r}_{pq}^{\boldsymbol{kl}} \hat{a}_{ij}^{pq} \right) \phi \qquad (2)$$

where $\hat{a}_{ij}^{\kappa\lambda}$ and $\hat{a}_{ij}^{pq}$ denote the usual excitation operators which substitute the internal orbital pair (φ_i, φ_j) by the general orbitals $(\varphi_\kappa, \varphi_\lambda)$ from a hypothetically complete orthonormal set, by the orbitals (φ_p, φ_q), respectively, from the given basis set. It was shown [2,5] that for $(\boldsymbol{k}, \boldsymbol{l}) = (i, j)$, $\phi_{ij}^{\boldsymbol{kl}}$ is equal to a term linear in r_{12} where the orbitals φ_i and φ_j in ϕ are joined and which is orthogonal to all the determinants of the traditional CI expansion. The additional terms where $(\boldsymbol{k}, \boldsymbol{l}) \neq (i, j)$ [6] ($\boldsymbol{k}$ and $\boldsymbol{l}$ run over all internal orbitals) are required to achieve the same invariance properties with respect to orbital rotations as in the corresponding traditional MR-CI. To distinguish the index pair $(\boldsymbol{k}, \boldsymbol{l})$ from the more physical pair (i, j), we follow the notation of Ref. [4] and write the former in bold face letters.

The ansatz Eq. (2), for each reference determinant contains $\propto N^4$ terms (N being the number of electrons), whereas there are only $\propto N^2$ electron pairs which form cusps in the wavefunction. Thus for large N, most of the terms are not well defined and in conjunction with inaccuracies due to numerics and the SA, this fact may give rise to serious instabilities (see Ref. [4] for a detailed discussion). Probably the simplest way to solve this problem is to restrict the r_{12}-terms to those that are absolutely necessary. For the treatment of molecular dissociation, this set consists of those terms that insure the invariance of the CI functional with respect to the unitary transformation of the molecular spin orbitals (obtained with MCSCF) to orbitals localized at the atomic centers. Invariance with respect to unitary transformations among the atomic orbitals, however, even if they belong to the same irrep (e.g. $1s$ and $2s$), seems dispensable. To this end, we form sets of spatial orbitals which contain exactly two members: a bonding orbital and its anti-bonding counterpart. Given an orbital index pair (i, j) we will let $(\boldsymbol{k}, \boldsymbol{l})$ run over all spin orbitals that can be constructed from the joined sets to which φ_i and φ_j belong. For example in a homo-nuclear diatomic (in D_{2h} symmetry) let $(\varphi_i, \varphi_j) = (1\sigma_g, 1\pi_{u,x})$. From these two orbitals we construct the two sets $\{1\sigma_g, 1\sigma_u\}$ and $\{1\pi_{u,x}, 1\pi_{g,x}\}$ and let $(\boldsymbol{k}, \boldsymbol{l})$ run over all spin orbitals that can be constructed from the members of the joined set, i.e. $\{1\sigma_g, 1\sigma_u, 1\pi_{u,x}, 1\pi_{g,x}\}$, where, of course, terms with a different spatial or spin symmetry as the state of consideration may be omitted. Since when using this approach the r_{12}-MR-CI wavefunction loses most of the invariance of rotations between pairs of inactive and respective active orbitals, it is now mandatory to properly define the internal orbitals. In the MCSCF calculations (where we use the same references as in the subsequent MR-CI(SD) or MR-ACPF expansion), we therefore fix the rotational degrees of freedom by requiring that the **F**-matrix in the space of the inactive orbitals and the **Q**-matrix in the space of the active orbitals [7] are diagonal.

The different types of matrix elements arising in an r_{12}-MR-CI may be simplified [2] using extensions of the well-known Slater-Condon rules. A priori no closed formulae result, however, in Ref. [2] it has been shown how these intermediate expressions may be evaluated; the final tensor products are listed in Table 3 of Ref. [5] and will not be repeated here. With the exception of the symbolic expression $g_{\kappa i''}^{pk''}\delta_\lambda^q$ (see Eq.(33) in Table 3 of Ref. [5]) which arises from the interaction of the r_{12}-terms with the determinants of the traditional CI expansion over the two-electron part of the Hamiltonian, all tensor products have storage requirements ($\propto N^6$ or $\propto N^2 n^2$, see Section 4.3 of Ref. [2]) which are easily fulfilled on present day computers. For the former expression, however, $\propto N^4 n^2$ elements have to be stored and manipulated, a task which at least requires some thought about efficient implementation. Fortunately, within the SA, only determinants with 2 external orbitals may interact with the r_{12}-terms. Since these matrix elements of the Hamiltonian occur in third order perturbation theory for the first time and since, in the presence of terms linear in r_{12}, one may expect a fast convergence of a perturbation expansion of the wavefunction in the cusp region, which has a small contribution (say $\approx 5\%$ of the correlation energy) when a basis set large enough to fulfill the SA is used, it seems justified to totally omit the mentioned matrix elements. To stay consistent, the corresponding matrix elements arising from the interaction of Slater determinants with r_{12}-terms over the one-electron part of the Hamiltonian (see Eq. (31) in Table 3 of Ref. [5]) also have to be omitted. Please note that in the single-reference closed-shell case, the Brillouin theorem may be used to avoid evaluation of the matrix elements mentioned.

The present r_{12} ansatz is easily combined with MR-ACPF [8] by appending the r_{12}-terms, Eq. (2), to the set of determinants which belongs to the external part of the correlation function (Ψ_e in Ref. [8]). This can be understood by noting that within the SA, the r_{12} ansatz, defined by Eq. (2), is equivalent to the ansatz of Ref. [2] where the summation is over only the virtual orbitals of the complete set. Thus the r_{12}-terms given by Eq. (2) may be regarded as consisting of a fixed linear combination of those double substitutions which are missing in the traditional CI expansion. Therefore, one may expect the r_{12}-MR-ACPF to qualitatively have the same (we have checked this numerically) size-extensivity properties (see Ref. [8]) as the corresponding MR-ACPF.

3. Details of implementation

The r_{12}-MR-CI(SD) and r_{12}-MR-ACPF methods have been implemented into the Columbus ''direct''-MR-CI program system [9] without abandoning its flexibility in defining the wavefunction and the possibility of making use of D_{2h} symmetry and subgroups. The special integrals [10] needed for the r_{12}-method have been implemented [11] into a recent version of program Hermit [12,13] which generates integrals over spherically harmonic Gaussians. The integrals over r_{12} are transformed to the molecular orbital (MO) basis with program Tran which is contained in the Columbus system; the $[r_{12}, T_1]$ integrals, however, where only two indices have to be transformed to external MOs, are computed by accumulating them in $\propto N^2 n^2$ words of memory using $\propto N^2 n^4$ floating point operations. The arrays needed to evaluate the matrix elements of the Hamiltonian $\boldsymbol{H}$ in r_{12}-CI are computed by a program called R12tran following the guidelines of Section 4.3 in Ref. [2].

We will now describe the changes made to program Ciudg, where finally the MR-CI(SD) or MR-ACPF equations are solved: to construct the r_{12}-terms according to Eq. (2), the reference configuration state functions (CSFs), which (as well as the others) in the GUGA formalism [14] are defined as Gelfand-Tsetlin states, are decomposed into Slater determinants. Based on these determinants, all possible r_{12}-terms defined by Eq. (2) are constructed. Of this initial set, redundant terms and (optionally) terms not required due to physical reasons (see Section 2) are removed. The matrix elements of the Hamiltonian between the r_{12}-terms are computed once. The entire diagonal elements and the elements of one (i, j) block are stored in sequential files, only the non-vanishing elements of the off-diagonal blocks are put to disc. The metric tensor $\boldsymbol{S}$ in the space of the r_{12}-terms is block-diagonal with respect to the (i,j) indices, the matrix elements depending on $(\boldsymbol{k}, \boldsymbol{l})$ only. Therefore one block of the metric tensor can easily be kept in main memory throughout the calculation. The interaction of the r_{12}-terms with the CSFs of the traditional CI expansion is computed by decomposing the latter into Slater determinants and generating a formula tape which contains the indices and weights of the tensors defined in Eq. (33) of Table 3 in Ref. [5] which are stored in arrays throughout the calculation. The programming of the evaluation of the matrix elements of the r_{12}-terms is considerably simplified by making heavy use of Fortran statement functions.

To minimize the changes made to the program code where the wavefunction is optimized, the coefficients $\boldsymbol{c}$ of the r_{12}-terms are defined in a symmetrically orthogonalized basis. Thus the $\boldsymbol{\sigma}$-vector is calculated by evaluating the expression

$$\boldsymbol{\sigma} := \boldsymbol{S}^{-1/2}\boldsymbol{H}\boldsymbol{S}^{-1/2}\boldsymbol{c} \tag{3}$$

from right to left. Since the condition numbers (defined as absolute largest eigenvalue divided by the absolute smallest eigenvalue) of $\boldsymbol{S}$ were usually found to be less than 10^3, this is a stable procedure. As described in Ref. [8] we use a modification of Davidson's method to optimize the wavefunction. To this end, a set of trial vectors is generated by a first-order update. To enhance convergence we compute the reduced resolvent in the block-diagonal approximation.

In the future, we will call the present software, where we additionally changed various details to enhance user friendliness, the Amica (''atoms and molecules in chemical accuracy'') suite of programs [15].

4. Applications

The basis sets we use in this work are based on the aug-cc-pV5Z basis set of Woon et al. [16]. The *s* set is re-contracted to $(15s)/[11s]$; the $(3g)$ set is substituted by the $(2g)$ set contained in aug-cc-pVQZ [17,18]; the tight *h* function is deleted. We logarithmically extrapolate a tight *d* function ($\eta = 11.911$). Our final (standard) basis set is $[11s9p6d4f2g1h]$ from which we construct three sets *spdf*, *spdfg* and (the unchanged) *spdfgh*.

We then investigated the influence of several changes made to the *spdf* set on the r_{12}-ACPF energies of the single atom and the molecule ($R = 2.07\,a_0$). We find the contraction errors ($\ll 0.1$ mE_h) are negligible on the level of (chemical) accuracy ($\approx$ 1 kcal/mol) we are aiming at. The substitutions of the *sp* part by Partridge's $[14s9p]$ and $[18s13p]$ sets [19] (while the diffusest *s* and *p* functions remain unchanged) lower the energies substantially (i.e. 0.2 and 0.5 mE_h, respectively for the atom and 0.7 and 1.4 mE_h, respectively for the molecule) resulting in a rising of D_e (which is computed as $2\,E(\mathrm{N}) - E(\mathrm{N}_2)$) by 0.1 and 0.2 kcal/mol, respectively. We have also done the substitution with the $[18s13p]$ set with the core electrons kept frozen and found that the lowerings of the individual systems (N and N_2) approximately halve; D_e, however, drops only by one fourth when compared to the value obtained with all electrons being correlated. Based on this findings, one would want to use Partridge's large *sp* sets. However this was not practical, since in our present program version the highest number of contracted basis functions is limited to 255. We therefore could not afford to use these large *sp* sets together with the *gh* sets. In the presence of the $[2g]$ set, however, the influence of the substitution of the standard *sp* set by the $[14s9p]$ set on the individual energies almost completely cancels in D_e which rises by only 0.03 kcal/mol. This finding seems to justify the usage of this (smaller) *sp* set, provided higher polarization functions are present.

The neglect of the most diffuse functions in the *spdf* set causes errors that are intolerable when one aims at chemical accuracy. The effect on the total energies and on D_e varies strongly, the diffuse *d* having the largest influence on the energies of both the atom (+0.7 mE_h) and the molecule (+1.6

mE_h). Its effect on D_e, however, almost cancels (−0.1 kcal/mol): here the neglect of the diffuse s increases D_e by 0.4 kcal/mol. To be on the safe side, we included diffuse functions of all occurring quantum numbers. A second set of diffuse functions, however, is dispensable since it raises D_e by only 0.09 kcal/mol. The presence of a tight d function is clearly mandatory: its neglect raises the energies of the atom by 0.4 mE_h and of the molecule by 1.8 mE_h, resulting in a lowering of D_e by 0.7 kcal/mol. In contrast, a second tight d function or a tight f function, as well as a second set of diffuse *spdf* functions are dispensable, since their influences on the individual energies are well below 0.1 mE_h.

To get a feeling for the overall quality of our standard basis set, we did an r_{12}-MR-ACPF calculation with 19 references generated by allowing for all possible single and double substitutions $2p \rightarrow 3p$, including those that do not have the symmetry (A_u in D_{2h}) of the state under investigation. Our result ($E_c = -187.852$ mE_h) is further lowered by 0.570 mE_h when Partridge's [18s13p] set is used as described above. The energy in the latter basis set only slightly (0.04 mE_h) overshoots a recent estimate [20] based on the evaluation of experimental data.

In Table 1 we have compiled the equilibrium energies (E_e), dissociation energies (D_e), equilibrium bond lengths (R_e) and harmonic frequencies (ω_e) computed for N_2 using various ansätze and basis sets. For our r_{12} ansatz we used those 20 references which contribute to the MCSCF wavefunction in the limit of large distances; see Ref. [21] for a listing. We validated this choice of the reference space in a comparison with a full-CI calculation in a DZP basis set with 6 electrons correlated [22]. MR-ACPF was found to underestimate D_e by 0.1 kcal/mol. Since this method is (at least approximately) size-extensive one may expect that this accuracy is conserved when all 14 electrons are correlated. Please note that the dissociation of N_2 is a rather easy case for this method since the molecule is closed-shell and in the separated atoms the spins of

Table 1
Comparison of calculated spectroscopic constants [a,b] of the ground state of $^{14}N_2$ with experimentally derived values [c]

Method	Corr. [d]	Basis set	$-E_e/E_h - 109$	D_e/(kcal/mol) [e]	R_e/Å	ω_e/cm^{-1}
r_{12}-MR-ACPF [f]	all	*spdf* [g]	0.535 479	−0.69(0.05)	+0.00013	+0.1
r_{12}-MR-ACPF	all	*spdfg* [g]	0.536 655	−0.16(0.09)	+0.00003	+1.8
r_{12}-MR-ACPF	all	*spdfgh* [h]	0.537 006	±0.00(0.12) [i]	+0.00009	+2.0
r_{12}-MR-ACPF	fc	*spdfgh*	0.418 670	−0.94(0.11)	+0.00226	−7.1
r_{12}-MR-CI(SD [f]	all	*spdfgh*	0.514 337	−0.58(0.13)	−0.00150	+15.8
r_{12}-MR-AQC [f]	all	*spdfgh*	0.532 963	−0.09(0.12)	−0.00024	+4.9
CCSD(T [j]	all	cc-pCV6Z	0.535 855	−1.13 [k]	−0.0007	+12.5
ICMRC [j,l]	all	cc-pCV5Z	0.509 547	−0.61 [k]	−0.0005	+8.8
ICMRCI + [j,l,m]	all	cc-pCV5Z	0.530 038	−1.82 [k]	−0.0005	±0.0
Experiment				228.42	1.09769	2358.6

[a] Entries are deviations from the experimental values given in the last line.

[b] Values of this work obtained from a fit of 5 equidistant points around 2.07 a_0 (0.05 a_0 mutual distance) to a 4th degree polynomial in $1/r$.

[c] Refs. [28,27].

[d] All 14 electrons are correlated (all); frozen core (fc).

[e] Dissociation energy corrected for BSSE (counterpoise correction in parenthesis).

[f] $\{2p\} \otimes \{2p\}$ orbitals active (6 electrons, 20 references in D_{2h}).

[g] Subsets of standard basis set.

[h] Standard basis set.

[i] Relativistic effects (≈ −0.2 kcal/mol) presumably cancel error; see text for details.

[j] From Ref. [26].

[k] BSSE was not corrected.

[l] $\{2s,2p\} \otimes \{2s,2p\}$ orbitals active (10 electrons, 176 references in D_{2h}).

[m] Davidson's correction applied.

the open-shell electrons are all parallel and therefore correlate to a lesser extent. MR-ACPF overestimates, e.g. the D_e of O_2 by 0.7 kcal/mol [8] compared to full-CI.

The first three lines of Table 1 demonstrate the fast convergence of the spectroscopic constants computed with r_{12}-MR-ACPF, to the experimental values. Using the *spdfgh* basis set results in D_e being accurate to within the experimental error, R_e is better than 10^{-4} Å and ω_e is accurate to 2 cm^{-1}. Only the D_e values were corrected for the basis set superposition error (BSSE) using the well-know Boys-Bernardi method, since even in the *spdfgh* set, the corrections to R_e $(+1.7 \times 10^{-5}$ Å) and ω_e $(+0.26\ \text{cm}^{-1})$ were found to be entirely negligible within the accuracy obtained. The BSSE *grows* with the highest l contained in the basis set, a behavior which presumably is due to higher polarization functions on one atom compensating the lack of saturation in the lower l shells on the other atom. Due to the fast l convergence of the r_{12} method, the further saturation and additional introduction of functions with higher l due to the ''ghost'' basis set seems to become unimportant. The coincidence of the computed D_e with the experimental value is probably due to a fortuitous cancelation of errors caused by unsaturations of the basis set with inherent errors of the ACPF method and relativistic effects. The latter were calculated [23] using CI(SD) with the Davidson correction for the N atom and CCSD(T) for the N_2 molecule, with the Dirac-Coulomb-Gaunt Hamiltonian in an uncontracted cc-pVTZ basis set with an augmented p function $(\eta = 283.8)$ and were found to *decrease* D_e by 0.2 kcal/mol (0.1 kcal/mol without the Gaunt interaction). Due to the smallness, we neglect these effects in the present work. There is both theoretical [24] and experimental [25] evidence that Born-Oppenheimer breakdown effects for molecules of similar mass as N_2 may safely be expected to be still several orders of magnitude too small to be of any importance for the present study. Comparing our calculated spectroscopic constants with recent (traditional) large-scale calculations [26] (see Table 1), we observe that our values are considerably closer to experiment [27,28].

To obtain the influence of the core correlation on the calculated spectroscopic constants, we performed an r_{12}-MR-ACPF calculation with the two core orbitals being doubly occupied in all CSFs and being omitted from the r_{12} terms. Our results $(\Delta D_e = +0.94$ kcal/mol, $\Delta R_e = -0.0022$ Å, $\Delta \omega_e = +9.1$ cm^{-1}, see Table 1) are in excellent agreement with recent estimate [26,29].

We also performed r_{12}-MR-CI(SD) calculations using the same 20 references as before. While D_e is still calculated to within chemical accuracy, the other spectroscopic constants are approximately ten times less accurate than the ones obtained with the corresponding ACPF ansatz. The results of the recently proposed alternative choice of the renormalization factor g in ACPF named ''averaged quadratic coupled-cluster method'' (AQCC) of Szalay and Bartlett [30] are, as expected, intermediate between the ACPF and CI values, the error in the spectroscopic constants being about two times larger than with ACPF. This behavior is connected to the wrong asymptotic dependence of AQCC; in that case $g \to 4/N$ instead of the correct relation for identical non-interacting electron pairs which is $g = 2/N$ as implemented in ACPF. Accordingly, the AQCC method recovers 99.3 % of the correlation energy obtained with ACPF, whereas the corresponding value for CI is only 95.8 %. While the slight difference in performance between ACPF and AQCC in many cases does not matter (AQCC may even be able to compensate for the tendency of ACPF to slightly overshoot correlation effects) when basis set saturation is the major bottleneck, it may become important at the basis set limit.

To assess the quality of the CCSD(T) and ICMRCI (with and without Davidson correction, denoted with ''+Q'') calculations of Ref. [26] we did MR-ACPF calculations in the cc-pCVxZ, $x =$ D,T,Q basis sets [31] and found the energies $(\approx -0.7\ \text{m}E_h)$ and D_e values $(< 0.2$ kcal/mol) to be in striking agreement with the ICMRCI + Q results, which in turn are close, i.e. better than 0.3 kcal/mol in D_e, to the CCSD(T) numbers. Comparing our MR-ACPF energy in the cc-pCVQZ set with the ICMRCI value of Ref. [26], we conclude that at the basis set limit the latter method, where 10 electrons (from $2s$ and $2p$) are active, resulting in 176 references in D_{2h}, will overestimate the D_e by 1.3 kcal/mol. We confirmed this number by a r_{12}-MR-CI(SD) calculation with these 176 references and obtained a BSSE corrected value which overshoots experiment by 0.6

kcal/mol. Adding the contraction error of this ICMRCI ansatz of +0.8 kcal/mol [29], we get an excellent agreement with our previous estimate. By similar arguments we conclude that the CCSD(T) and ICMRCI + Q methods of Ref. [26] in the basis set limit underestimate D_e by 0.3 (in excellent agreement with the extrapolations of Ref. [32]) and 0.04 kcal/mol, respectively. This implies that the basis set incompleteness error of CCSD(T) in the cc-pCV6Z set [26] which gives an energy too low by 1.1 kcal/mol is 0.8 kcal/mol which is in excellent agreement with the estimate (0.7 kcal/mol) of Ref. [29]. However, using this basis set with e.g. ICMRCI + Q which, due to a fortuitous cancelation of errors in the correlation treatment, (in the large L limit) is accurate to better than 0.1 kcal/mol (see above), in the cc-pCV6Z set an accuracy better than 1 kcal/mol can presumably still not be achieved since the BSSE for a cc-pV6Z set with a frozen core was still found to be 0.2 kcal/mol [29].

We also computed D_e with r_{12}-MR-ACPF using 176 references, obtaining a value too low by 1.2 kcal/mol, which is in good agreement with the 1.0 kcal/mol energy lowering obtained by Almlöf et al. [33] on going from MR-ACPF with 6 active electrons (32 references) to the ansatz with 10 active electrons (176 references). This puzzling behavior may be explained by an imbalance caused by a double counting of certain terms in the expansion of the wavefunction. To avoid this phenomenon when using ACPF, the reference space should not be too large: we recommend a minimal space constructed by chemical arguments which may be appended by certain CSFs to allow for the presence of higher linked terms in the cluster expansion (e.g. see the calculation of the N atom above). These problems are less apparent if ACPF is used in conjunction with internal contraction (see Ref. [26]) since here, the weight of superfluous terms is kept low by constraints.

After having established the high accuracy (see above) of r_{12}-MR-ACPF with 20 references in the standard *spdfgh* basis set (250 functions), we decided to compute the whole potential energy curve in the range of chemical distances with this ansatz (see Table 2). All computations were performed on a Silicon-Graphics ''Power-Challenge'' (R8000, 75 MHz). The timings for the calculations, e.g. at an interatomic distance of 2.07 a_0 were: 1.8 h for the integrals and their transformation, 1.3 h for the computation of the special matrix elements needed by the r_{12} method and 3.9 h for the 10 iterations needed to converge the r_{12}-MR-ACPF energy to better than 10^{-6} E_h, resulting in a total CPU time (without the optimization of the orbitals which took 1.5 h from scratch) of 7.0 h. This number is to be compared with 0.5 h used for the integrals and their transformation and 3.3 h for 10 iterations of the corresponding (traditional) MR-ACPF, resulting in a total CPU time (without orbitals) of 3.8 h. The computation of the counterpoise correction, where the integral handling is the most time consuming step, (without the SCF which took 0.8 h from scratch) we used 4.1 h CPU time for the r_{12}-ACPF calculation; the corresponding traditional computation would take 1.2 h.

Table 2
r_{12}-MR-ACPF energie [a] and BSSE [b] for the ground state of N_2

R/a_0	$-E/E_h - 108$	$-BSSE/\mu E_h$
1.4	0.650 991	225
1.6	1.215 183	214
1.8	1.456 391	208
1.9	1.508 642	204
1.97	1.527 753	200
2.02	1.534 651	198
2.07	1.536 991	195
2.12	1.535 565	193
2.17	1.531 054	190
2.22	1.524 037	188
2.3	1.508 811	184
2.5	1.458 140	172
2.75	1.387 836	158
3	1.323 866	146
3.5	1.234 660	117
4	1.194 726	92
5	1.176 512	58
6	1.173 851	39
100	1.172 808	0

[a] 20 reference CSFs and minimal r_{12}-ansatz for proper dissociation; all electrons correlated; $[11s9p6d4f2g1h]$ basis set as specified in the text.
[b] BSSE computed with the counterpoise method.

We then interpolated the curve (including corrections for the BSSE) between neighboring points using cubic splines, the limits of small and large distances were extrapolated using an exponential and a rational function, respectively and finally numerically solved the Schrödinger equation of the rotating

Table 3
Comparison of calculate [a] spectroscopic constant [b] of the ground state of $^{14}N_2$ with experiment

	Present work	Experiment
$B_0 - B_1$	0.01733	0.0173697(30) [c]
$B_1 - B_2$	0.01746	0.0174331(35) [c]
$D_1 - D_0$	9.5×10^{-9}	$1.04(0.16) \times 10^{-8}$ [c]
G_0 [d]	1176.4 [f]	1175.767 [e]
ω_e	2360 [f]	2358.57 [g]
$\omega_e x_e$	14.35 [f]	14.324 [g]
B_e	1.9979 [h]	1.99824_1 [g]
α_e	0.01733 [h]	0.017318 [g]
D_e [i]	5.73×10^{-6} [j]	5.76×10^{-6} [g]
R_e/Å	1.0978 [k]	1.09768_5 [g]

[a] From T_v, B_v and D_v computed from the potential energy curve (including corrections for BSSE) listed in Table 2.
[b] If not stated otherwise, in units of cm^{-1}.2e[c] From Ref. [35]; the numbers in parenthesis give three times the standard deviation.
[d] Zero point energy.
[e] From Ref. [27].
[f] By solving $T_v = -G_0 + \omega_e(v + \frac{1}{2}) + \omega_e x_e(v + \frac{1}{2})^2$ for $v = 0,1,2$.
[g] From Ref. [28].
[h] By solving $B_v = B_e - \alpha_e(v + \frac{1}{2})$ for $v = 0,1$.
[i] Centrifugal distortion constant.
[j] By solving $D_v = D_e + \beta_e(v + \frac{1}{2})$ for $v = 0,1$.
[k] Calculated as $R_e = \sqrt{h/\left(8\pi^2 c\mu B_e\right)}$.

and vibrating molecule using Cooley's method, implemented in the program Level [34] in order to obtain the vibrational levels T_v, rotational constants B_v and centrifugal distortion constants D_v. Our T_v differ from the first 22 experimentally derived values listed in Table 78 of Ref. [27] (about the first half of the well depth) by at most $+10$ cm^{-1}, compared with Table 49 of Ref. [27] our B_v are at most 20 cm^{-1} too large, our D_0 value of 5.73×10^6 cm^{-1} compares favorably with the values (5.48 ± 0.05, 5.76 ± 0.03 and 5.743×10^6 cm^{-1}) of Ref. [27] and our D_1 is 1×10^4 cm^{-1} to large. From these T_v, B_v and D_v values we computed various spectroscopic constants (see Table 3). A satisfying agreement with experimentally derived values is achieved: the accuracies obtained in the present work vary from being in the same range as the experimental accuracy to (at most) 100 times worse.

5. Summary and conclusions

To overcome the basis set bottleneck in CI calculations, we have programmed an MR-CI(SD) method which contains terms that are linear in the interelectronic distances (r_{12}). In order to accurately solve the electronic Schrödinger equation, we combine this method with the (approximately) size-extensive MR-ACPF which is able to yield energies close to the full-CI limit. To demonstrate the high performance of the present method and to show that it can be applied to general chemical problems, we have computed the potential energy curve of the nitrogen dimer (N_2) to an accuracy which is probably out of reach using traditional CI methods on present day computers without the aid of extrapolations or empirical corrections (see e.g. Ref. [32]).

This high accuracy is not only useful for the calculation of atomic and molecular spectra; other applications are the computation of potential energy surfaces, e.g. of elementary chemical reactions and the generation of benchmarks to be used for the calibration of density functional methods.

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