General contraction of Gaussian basis sets. II. Atomic natural orbitals and the calculation of atomic and molecular properties

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Abstract

Our recently proposed scheme for using natural orbitals from atomic CI wave functions as a basis set for LCAO calculations is extended for the calculation of molecular properties. For one-electron properties like multipole moments, which are determined largely by the outermost regions of the molecular wave function, it is necessary to increase the flexibility of the basis in these regions. This is most easily done by uncontracting the outermost Gaussian primitives, and/or by adding diffuse primitives. A similar approach can be employed for the calculation of polarizabilities. Properties which are not dominated by the long-range part of the wave function, such as spectroscopic constants or electric field gradients at the nucleus, can generally be treated satisfactorily with the original ANO sets.

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I. Introduction

In a recent paper [1] (referred to hereafter as I) we proposed the use of truncated sets of atomic natural orbitals (ANOs) as basis functions for molecular calculations. ANOs provide very compact basis sets that can recover a large fraction of the correlation energy in molecular calculations. In practical applications, the ANOs are expanded as general contractions of Gaussian functions: the size of the contracted basis set is the limiting factor that determines the feasibility of an accurate correlated calculation, whereas the primitive set only affects the integral evaluation time, which is usually of minor significance.

It was shown in I that ANO basis sets yield very small contraction errors (defined as the difference between a result using a contracted basis and the result obtained with the uncontracted primitive set) for both SCF and CI energies, in molecules as well as in the atoms. This is in agreement with earlier studies by Petersson *et al.* (see Ref. 2 and references therein), using pair-natural orbitals. Similar conclusions can also be inferred from a study by Davidson and Feller [3], who used a double-zeta ANO basis in a set of calculations comparing different basis sets for the water molecule. Two particularly important conclusions can be drawn from the work presented in I: first, that the occupation numbers of the atomic natural orbitals (ANOs) provide a very simple and reliable criterion for determining the size of contracted basis sets to be used when a particular accuracy in the energy is required, and, second, that large sets of primitive functions can be contracted using ANOs with essentially no loss in the correlation energy. This permits the use of large primitive polarization sets that effectively saturate the space for a given angular quantum number without the size of the contracted basis

becoming unmanageably large. However, while ANOs clearly provide a route to minimum contraction loss and efficient use of large primitive sets as far as total energies are concerned, it is not clear that they will be as suitable for the calculation of molecular properties. The requirements on a basis set to yield good properties may be different (depending on the property) from those for calculating good energies.

Some properties, such as multipole moments or polarizabilities, depend crucially on the outermost regions of the charge density. It is, of course, well known that to achieve high accuracy in such properties it is necessary to augment energy-optimized primitive sets with diffuse functions (including diffuse polarization functions). Consequently, a contraction procedure such as the ANO prescription of I, which is designed to minimize the contraction error in the total energy when contracting an energy-optimized primitive set, is unlikely to yield good values for these properties without some modification. One obvious approach to increasing the flexibility in the outer part of the wave function is to add (uncontracted) diffuse primitives to the ANO contracted sets. It will usually be the case, however, that the most strongly occupied ANOs will contain only a small contribution from the most diffuse primitives in the original basis, and it may be necessary to uncontract the outermost primitives in the ANO set. In fact, as will be seen below, this latter step is probably all that is required to essentially eliminate contraction loss in dipole moments. For higher multipole moments further augmentation of the basis is desirable. Of course, the contraction procedure is unaffected by such further augmentation. Some aspects of these modifications to ANO contractions have been discussed previously [4,5].

Contraction errors in spectroscopic constants and molecular structures can be expected to be small in basis sets which yield small contraction errors

in the total energies. The original ANO procedure is therefore expected to perform well for such quantities: this hypothesis is supported not only by the comparisons with uncontracted calculations shown below, but also in a number of recent applications (see, for example, Ref. 6 and references therein). A property such as electric field gradient at the nucleus (EFG), which shows an r^{-3} dependence, but whose inner-shell contribution tends to average to zero because of the near-spherical shape of the inner-shell charge distribution, is dominated by the inner part of the valence charge distribution. It might therefore be expected that an ANO set would yield little contraction loss in EFGs, and this is generally borne out by our results.

Our purpose in the present work is to discuss in detail the performance of ANOs in property calculations as we did previously for the total energy, and we will therefore concentrate on primitive basis sets like those used in I. These sets are certainly large enough to saturate the radial expansion for every l-value considered, and in some cases may be larger than necessary. It is entirely plausible that by careful optimization of polarization exponents ANOs could be expanded in smaller primitive polarization sets. Dunning [7] has recently investigated the alternative of using uncontracted *optimized* primitive polarization sets and additional valence basis functions. This approach may provide an economic alternative to ANO basis sets.

In the following section we briefly discuss the computational methods used, then in section III results of contraction losses in properties are given for the molecules H_2O, HBr, N_2, and OH, and for Ne atom. Section IV contains our conclusions. It should be understood that our aim in these investigations is to show how to reduce the contraction error incurred when large primitive basis sets are used in accurate molecular calculations. With a segmented contraction scheme, a rather flexible contraction is usually

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required. In this work, we consider only segmented sets of the same size as the generally contracted ones, since a larger size would make the former unfeasible for a high-quality correlation treatment. For example, a primitive set such as $(13s\ 8p)$ for a first-row atom can be contracted to $[8s\ 6p]$ using a segmented contraction with a very small contraction error, but this is a much larger basis than a $[5s\ 4p]$ ANO contraction that gives a smaller contraction error in the total energy. We will not consider such segmented sets. Also, while it can be expected that basis sets of the quality we consider, when used with suitable treatments of electron correlation, will give very reliable estimates of molecular properties, it is not the purpose of this work to compare results with experiment or with other calculations. We concentrate here exclusively on the issue of contraction error.

II. Computational methods

The method used for obtaining the ANO contraction coefficients has been described in detail in I. A single-reference single and double excitation CI (SDCI) calculation is performed on the ground state of the desired atom in the chosen primitive basis set. Only the valence electrons of the atom are included in the correlation treatment in the present work. The natural orbitals from this SDCI wave function, ordered by decreasing occupation numbers, are then used to define the contraction coefficients. Symmetry and equivalence restrictions are imposed on the ANOs [8]. Primitive basis sets from a number of sources have been used and these are identified in section III below. The conventional notation for contracted basis sets has been extended here: $[5+1s \; 4+1p \; 3+1d]$ indicates a contracted basis comprising 5 s-type ANOs and the outermost primitive s function uncontracted, etc. Supplementary diffuse functions are always added uncontracted: the addition of two diffuse s primitives and one diffuse p primitive is denoted $+ (2s \; 1p)$.

All calculations were performed with the MOLECULE–SWEDEN [9] program system, running on the NASA Ames CRAY X-MP/48 or the Minnesota Supercomputer Center CRAY 2. Molecular geometries are given in the text or tables for each species studied. All basis sets comprised pure spherical harmonic basis functions. One-electron properties have usually been computed as expectation values of the appropriate operators; higher-order properties like polarizabilities have been computed as energy derivatives

The analysis of results is complicated by the number of properties computed here. In I it was possible to judge the performance of a given basis

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set from just the computed energy. While it is possible to examine a range of properties, it would hardly be feasible to publish all of the data required, at least for the extensive study of H_2O and HBr presented below. We have therefore proceeded via an alternative approach, which draws on a scheme for estimating basis set quality devised by Maroulis and co-workers [10]. Consider a set of N properties obtained in n basis sets:

$$\{Q^\alpha_i: i = 0,... n-1; \alpha = 1,... N\}$$

Here i indexes basis sets, with $i = 0$ being a chosen "reference" set (say, the uncontracted basis), while each Q^α is a different property, such as energy, dipole moment component, polarizability tensor component, etc. All properties are evaluated at the same level of wave function, such as SCF, SDCI, or indeed a correlation contribution given by the difference between the two. We can form the set of differences $\{P\}$ where

$$P^\alpha_i = Q^\alpha_i - Q^\alpha_0 \quad \forall\, i,$$

so that the reference values are all zero, and then scale these differences as

$$J^\alpha_i = P^\alpha_i / \max_\alpha (P^\alpha_i) \quad \forall\, i.$$

Hence the "worst" result for a particular property (that is, the result that deviates most from the reference result), has a J^α_i value of one, while the reference result has a J^α_i value of zero. We can regard the set $\{J^\alpha_i : \alpha = 1, ...$

N} as the elements of a vector $\mathbf{J}_i$ for each basis i, and thus regard the (scaled) norm

$$\mathcal{J}_i = N^{-1} \, \| \mathbf{J}_i \|$$

as a single measure of quality for basis set i, as $\mathcal{J}_i$ essentially represents the "distance" between the reference basis and basis i for the particular set of properties. Hence the smaller is $\mathcal{J}_i$, the better the agreement between basis i and the reference basis. If the latter is the uncontracted basis, $\mathcal{J}_i$ then immediately gives a measure of the contraction error for the set of properties considered The treatment of Maroulis *et al.* goes beyond this level by using logarithms of J^α_i values, in which case the reference values become infinite, in order to make contact with information theory, but such elaborations are unnecessary for our purpose.

The comparison of basis sets by $\mathcal{J}_i$ values is very simple, as the results can conveniently be presented as column graphs of a set of values {$\mathcal{J}_i$: $i = 1,n$}. In addition, it is possible to consider subsets of the overall set of properties for comparison purposes. For example, it may be desirable to know not only how well a basis performs for all properties computed, but also for a selected subset such as multipole moments or polarizabilities. It is only necessary to restrict the range of α used in computing {$\mathcal{J}$} to generate this information.

III. Results and Discussion.

A. H$_2$O one-electron properties

The oxygen atomic basis sets are derived from van Duijneveldt's (13s 8p) primitive set [11], augmented with six d functions forming an even-tempered sequence ($\alpha\beta^k$, $0 \leq k \leq 5$) with $\alpha = 0.13$ and $\beta = 2.5$, and an even-tempered sequence of four f functions ($\alpha = 0.39$, $\beta = 2.5$). The primitive hydrogen basis set is the (8s 6p 4d) basis given in I. The ANO contractions are based on natural orbitals from an SDCI wave function for ground-state oxygen atom and for the hydrogen molecule (see I). It should be noted that when results for "segmented" contractions are quoted, the sp basis for O and s for H comprise one contracted function of each symmetry (using van Duijneveldt's SCF coefficients) and the outermost primitives uncontracted, while for the higher angular functions the contraction pattern is the same but the coefficients are taken from O or H$_2$ natural orbitals. The oxygen atom is positioned at the origin, with the hydrogen atoms at coordinates ($\pm$1.43153,0,1.10941), and all property values quoted are relative to the origin. Different contraction schemes are labelled according to Table 1.

It is not feasible to present results for all properties and all basis sets in tabular form, so we quote results for a few properties in Tables 1 and 2 and use column graphs of $\{\mathcal{J}\}$ values, as discussed in section II, for the full comparisons. Since the reference values were obtained with the uncontracted basis, the figures show the contraction error for each contracted basis. In the tables we give SCF and SDCI results for the uncontracted basis (labelled U)

and then for each contracted basis we give the contraction error. The figures show in addition the correlation contribution (the difference between the SDCI and SCF results). This is useful in identifying cancellations between SCF and correlation errors. Fig. 1 is based on $\{\mathcal{J}\}$ values for the following properties: energy, electric field and electric field gradient at the nuclei, dipole and quadrupole moment, diamagnetic susceptibility, the mass-velocity and Darwin relativistic energy contributions [12] and the potential at the set of points $\{(0,0,-Z): Z = 2, 4, 6, 10\}$. Fig. 2 compares "point" properties: potential at the aforementioned points and electric field and electric field gradient at the nuclei, while Fig. 3 compares only the permanent moments (dipole, quadrupole and octopole). Optimum geometries were obtained with SDCI wave functions, but apart from the smallest contracted sets — [$3s\ 2p\ 1d/2s\ 1p$] ANO and segmented (sets F and I, respectively) — all the results were so close to the uncontracted basis values (within 0.005 a_0 in bond length and 0.3° in angle) that no meaningful comparisons can be made.

The energy results are similar to those discussed in I. Replacing the ANOs with the lowest occupation numbers by the outermost primitive uncontracted generally improves the SCF energy somewhat but makes the correlation energy worse. The addition of diffuse functions (basis C) does not significantly affect the energies, as expected. From Table 1 it can be seen that the largest contracted sets: ANO sets A and B and segmented set G, perform about equally well for potential and for electric field gradient at the nuclei, the ANO sets give better EFG results for H and the segmented set better results for O. The comparison in Fig. 2 shows that the correlation contribution error for set A is larger than that for set B, so uncontracting the outermost primitive has some effect on these properties.

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Again, as expected, these properties are unaffected by the addition of diffuse functions.

The correlation errors for the smaller sets D and E are similar, but set E has a smaller SCF contraction error and thus a lower SDCI error, as can be seen in Fig. 2. Set H performs similarly to set D at the SCF level, but has a much larger correlation contraction error. The smallest sets, F and I are not satisfactory for any of these properties and show large contraction errors even at the SCF level. For the point properties there is much less disparity among the correlation contraction errors than among the corresponding SCF values, as seen in Fig. 2. This suggests that the contraction error in these properties converges more slowly than does the correlation energy itself. It is likely that better O EFGs, for example, would require including more ANOs, or perhaps using a modified ANO basis set such as [5+1s 4+1p 3+1d 2f/4+1s 3+1p 2d]. A similar conclusion is drawn for HBr in the next section.

Table 2 contains values for various multipole moments of H_2O. In addition to the quadrupole moment, we have included one component of the diamagnetic susceptibility tensor χ. In combination with the two independent components of the quadrupole moment tensor (Θ) we give, this defines all non-vanishing second moments. We also give the two independent components of the octopole moment tensor Ω. Fig. 3 shows a comparison of $\{J\}$ values for all non-vanishing components of the multipole moments and the diamagnetic susceptibilities. The figure illustrates the inadequacy of the smallest sets, F and I, and also of set D, the [4s 3p 2d 1f/3s 2p 1d] ANO set. The contraction error in the correlation contribution for set A, the [5s 4p 3d 2f/4s 3p 2d] ANO set is also large, but this appears to be partly cancelled by SCF contraction errors. Clearly, the best results are obtained

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with large sets in which the outermost primitives are uncontracted, although surprisingly Fig. 3 indicates that set E is superior to the larger set B, obtained by a similar prescription. The contraction errors in the octopole moments for set E are substantially smaller than for set B, which is unexpected, and even when diffuse functions are added to set B to give set C the same surprising conclusion holds. This observation may derive from a cancellation in errors in the values of the Cartesian third moments computed with set E.

Fig. 1 shows a comparison of the different basis sets for all the properties computed (including the energy). Overall, sets A, B, C, and G perform best, with little to choose between them if all properties are of interest. The energies obtained with the segmented contraction of set G are inferior to those of the other three sets, but set G produces better multipole moments. Sets A and B are the same size as set G, but the modified ANO contraction scheme of set B, with the outermost primitive uncontracted is clearly superior to A for multipole moments, while giving very similar energies to A (and much better energies than G). If both energies and multipole moments are of interest set B appears to offer the best compromise. The smaller sets, D, E and H, show larger contraction errors overall, although not by much in the case of set E. These sets appear to be the smallest that can be used reliably, as the contraction errors for sets F and I are unacceptably large.

B. HBr one-electron properties

The primitive atomic *spd* basis set used for Br is derived from Dunning's (14*s* 11*p* 5*d*) set [13]. The outermost two *p* primitives were replaced by four primitives with exponents 0.7052, 0.3026, 0.1299, and 0.0557, and the *d* space was augmented with two diffuse *d* primitives (exponents 0.4390 and 0.1463). Four *f* sets were added, with exponents chosen as an even-tempered sequence ($\alpha\beta^k$, $0 \leq k \leq 3$) with $\alpha = 0.13$ and $\beta = 2.5$. The primitive set for H was the (8*s* 6*p* 4*d*) basis used for H_2O above. The SDCI calculations performed on HBr involve correlation of the eight valence electrons only. The bond length used was 2.673 a_0, the experimental equilibrium value [14]. The contraction schemes used in the comparisons are labelled and identified in Table 3. A first set of ANO contractions was based on Br ANOs, with uncontraction of the outermost primitives in some cases. A second set of ANO contractions was based on ANOs obtained by averaging the density matrices for SDCI calculations on Br and Br⁻; again, some sets feature uncontracting the most diffuse primitives. In addition to comparing with a basis set obtained from Raffenetti's approach to general contraction [15] (that is, the use of atomic SCF orbitals), we have also generated a segmented basis set for Br. This is not straightforward for a set of this size (as noted previously by Dunning [13], who recommended using a general contraction), and certainly cannot be satisfactorily achieved without duplication of some primitives in different contracted functions unless much larger contracted sets are tolerated.

Column graphs of $\{J\}$ values for these various sets are given in Figs. 4-6. The properties used in generating the first of these graphs comprise total energies, dipole, quadrupole and octopole moments, EFGs at the nuclei, electric field at the nuclei, diamagnetic susceptibility, and the

mass-velocity and Darwin contributions to the first-order relativistic correction to the energy. Only property values distinct by symmetry (and by trace conditions on operators) were included. In addition to considering all properties, as for H_2O above we consider also the subset of $\{\mathcal{J}\}$ values obtained from only the electric moments, and from only the "point" properties, which for HBr comprise EFG and electric field at the nuclei.

The multipole moment results obtained with various basis sets are listed in Table 3. Again, the uncontracted results are given explicitly and only the contraction errors are given for the contracted basis sets. For the dipole moment all of the basis sets show only small contraction losses in both the SCF and correlation contributions. For the quadrupole and octopole moments there are larger differences between the various sets and larger contraction errors. The largest contracted basis, set C, produces the smallest contraction errors, and is the only set that accurately reproduces the uncontracted SCF and correlation contributions to Ω_{zzz}. The set contracted using Raffenetti's prescription for Br and ANOs (from H_2) for H is unsatisfactory at both the SCF and CI levels, although this appears to be a problem mainly with combining the different contraction schemes, as the results obtained when Raffenetti's prescription is used for both Br and H are fairly good. Possibly the ANO hydrogen basis is too compact to provide a balanced description of the charge distribution when combined with the flexible Br Raffenetti contraction.

Averaging the ANOs for Br and Br^- produces a basis set in which the radial maxima of the valence orbitals occur at larger r than those in Br, and it might be hoped that such a basis set would provide a more flexible description of the outer region of the electron density. This does not appear to be the case in HBr, where such a basis shows no particular advantage over

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the Br ANOs for multipole moments. In fact, set G, obtained from averaged ANOs, is inferior to that obtained from Br ANOs (set A). Evidently, bromine in HBr is more similar to neutral Br than to Br$^-$, as suggested by a point dipole approximation to the dipole moment, and it appears that there is no useful gain in flexibility for multipole moment calculations from using averaged ANOs. Of course, for calculations on more ionic species this would probably not be the case. Overall, only the modified ANO contractions are satisfactory for the higher multipole moments, as Fig 5 also shows, but (in contrast to H_2O above) the segmented contraction, set E, is no better than the modified ANO contractions B or C, despite the flexibility obtained by having a number of the outermost primitives uncontracted. Further, there is some evidence that the performance of the segmented contraction may derive from a cancellation of errors: the segmented basis results for the diamagnetic susceptibility χ_{zz} are the worst of any of the contraction schemes, and this property is simply a different combination of second moment integrals from Θ_{zz}.

The results for EFGs show more consistent trends than do the multipole moment results, as can be seen from Fig 6: all of the contracted sets reproduce the uncontracted basis EFG values at H very well, and none of the contracted sets are satisfactory for the Br values, at least not at the SCF level. The segmented basis E gives the worst results, but even the largest ANO set, C, shows a discrepancy of 4% with the uncontracted result. Again, as expected from the r^{-3} form of the operator and as observed above for H_2O, uncontracting the outermost primitives does little to improve the result, at least if this function replaces an ANO. Thus again the basis set contraction requirements for EFGs are seen to be quite different from those for multipole moments. While set C gives the best agreement with the

uncontracted results. It is likely that an [8s 7p 5d 3f/5s 4p 3d] set consisting entirely of ANOs would perform even better. Finally, as the ANOs are defined by a calculation in which only the Br valence electrons are correlated, their ability to describe the innermost valence and outermost core regions is compromised. ANOs defined by a calculation in which the M shell is also correlated could perform much better in this regard, but the size of the resulting basis would probably be impractically large — additional d and f primitives would have to be included, etc.

The energy results obtained for HBr are also listed in Table 3. The contraction loss at the SCF level is small for all sets except the segmented contraction; this error is almost entirely the contraction error in Br. The contraction loss in the correlation energy is small for all sets, although the ANO contractions are always superior to those obtained by Raffenetti's prescription, or the segmented set. The first-order perturbation theory contribution from relativistic effects [12] shows rather small contraction losses at the SCF level, except again for the segmented set. The rather larger errors observed using the Raffenetti contraction are probably due to the fact that these sets are not as flexible in the inner valence region of Br as the ANO sets as the functions beyond the occupied SCF space are simply the outermost primitives. Thus these sets might be expected to perform better than ANO sets of the same size for properties such as multipole moments, but worse for properties such as IPs or the relativistic contribution, as observed. Finally, we have computed the two lowest ionization potentials (IPs) of HBr using all basis sets used in Table 3. All of the contracted sets yield very small contraction errors (less than 0.01 eV) in these IPs and little useful comparative information can be deduced from the results.

C. OH $X^2\Pi$ dipole moment function

The dipole moment of OH in its ground ($^2\Pi$) state has a maximum value at a considerably larger internuclear separation than equilibrium. The dipole moment function and potential curve were recently investigated [16] using multireference CI (MRCI) wave functions and an extended [5s 4p 3+1d 2f 1g/4s 3p 2d] + (1s 1p) (on O) basis. In order to investigate the performance of different modified ANO contraction schemes, we have computed the dipole moment function and potential curve with several different basis sets. All are derived from the same (13s 8p 6d 4f) + (1s 1p) primitive set on O and (8s 6p 4d) set on H. This set differs from the primitive set used to construct the basis of Ref. 16 only in the omission of g functions. The reference space for the MRCI was the same as that of Ref. 16.

Spectroscopic constants and dipole moment function results for OH are given in Table 4. The maximum value of the dipole moment is denoted μ_{max}, and the internuclear separation at which this maximum occurs is denoted $r\mu_{max}$. The spectroscopic constants for all contracted sets are in good agreement with the uncontracted set. The contraction loss in the dipole moment maximum value is very small for those sets with increased flexibility in the outermost region: only the unmodified [5s 4p 3d 2f/4s 3p 2d] set, which omits the diffuse (1s 1p) set on O, shows a perceptible difference. On the other hand, $r\mu_{max}$ is more sensitive to contraction. The [4+1s 3+1p 3+1d 2f/4s 3p 2d] + (1s 1p) set, in which the most weakly occupied s and p ANOs are replaced by the outermost primitive uncontracted, has a slightly reduced contraction error relative to the original

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$[5s\ 4p\ 3+1d\ 2f/4s\ 3p\ 2d] + (1s\ 1p)$ set, but there is still a difference of almost 0.01 a_0 in $r\mu_{max}$ with the uncontracted result. This suggests that there is a contraction error of some 0.008 a_0 in the $r\mu_{max}$ value of Ref. 16, which is consistent with the estimate there that the computed value was 0.007 a_0 too large [17]. The importance of uncontracting the outermost d primitive is discussed further in Ref. 17, where it is shown that the absence of diffuse d functions has a noticeable effect on the dipole moment function. For example, the $3d$ primitive set of Dunning [7] requires augmentation with a diffuse d to correctly predict the slope of the dipole moment at r_e.

The OH results provide further support for the conclusions drawn above for H_2O that good results for properties such as dipole moments can be obtained by uncontracting the outermost primitive and/or by adding a diffuse sp set. As a final note on OH, we have investigated whether basis set contraction affects the difference between a dipole moment computed as the expectation value of the dipole operator, and as the first derivative of the energy with respect to an applied field. For the uncontracted basis, these two approaches give MRCI dipole moment values that differ by 0.0028 a.u. at $r = 2.2\ a_0$. The $[4+1s\ 3+1p\ 3+1d\ 2f/4s\ 3p\ 2d] + (1s\ 1p)$ set shows the same difference between the two approaches, while with the $[5s\ 4p\ 3+1d\ 2f/4s\ 3p\ 2d] + (1s\ 1p)$ set the difference has increased slightly, to 0.0030 a.u. Such differences are sufficiently small that is difficult to draw firm conclusions about the effect of basis set contraction, except that they appear to be very small for sets of this size.

D. Polarizabilities of Ne, N_2 and H_2O

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Up to this point we have considered only the calculation of first-order properties. For higher-order electric properties the requirements on primitive basis sets are very demanding [18], quite apart from any considerations of basis set contraction. We have therefore investigated the electric susceptibilities of the neon atom, with attention both to the construction of primitive sets and their contraction. All calculations were carried out using finite perturbation methods, applying fields and field gradients of various strengths to yield the static dipole polarizability, dipole hyperpolarizability, dipole-dipole-quadrupole hyperpolarizability, and the quadrupole polarizability. The values are reported according to Buckingham's definitions [19] for the mean polarizability (α), second hyperpolarizability (γ), dipole-dipole-quadrupole hyperpolarizability (B) and quadrupole polarizability (C). Results are reported for both SCF and SDCI wave functions; only the eight valence electrons were correlated in the latter.

All of the contraction schemes investigated were based on the (13s 8p) primitive set of van Duijneveldt [11], augmented with six d functions forming an even-tempered sequence ($\alpha\beta^k$, $0 \le k \le 5$) with $\alpha = 0.20$ and $\beta = 2.5$, and an even-tempered sequence of four f functions ($\alpha = 0.61$, $\beta = 2.5$). All sets were augmented with an uncontracted (2s 2p 1d 1f) diffuse set with exponents ($\alpha_s = 0.12$ and 0.048, $\alpha_p = 0.064$ and 0.0256, $\alpha_d = 0.08$, and $\alpha_f = 0.24$). SCF and SDCI energies were computed in the presence of combinations of fields of strength 0.005, 0.001 or 0.002 a.u and field gradients of strength ±0.0025 or 0.005 a.u. and fitted to a functional form from which the polarizabilities were obtained.

For the mean polarizability α the larger segmented set shows the smallest contraction error, although this set overestimates the correlation contribution to α. The smaller segmented set gives polarizability contraction

errors smaller than the ANO set of the same size, but larger than any of the larger ANO sets. The modified ANO contraction scheme of the [4+1s 3+1p 2+1d 1+1f] + (2s 2p 1d 1f) set yields small contraction errors for γ, B, and C, similar to those of the larger segmented contraction, with the benefit of much less contraction error in the energies. It is clear from the results of Table 5 that the unmodified ANO contraction scheme, even when the diffuse (2s 2p 1d 1f) set is added, is not capable of yielding an acceptable contraction error in polarizabilities. This is consistent with the observations above in the context of molecular multipole moments.

In order to ensure that the conclusions drawn about the polarizabilities of Ne carry over to molecules, we have determined the dipole polarizability tensor for the molecules N_2 and H_2O. Because of the lower symmetry and larger number of tensor components that must be determined, it is not possible to use primitive sets as large as those employed in the calculations described in this work up to this point. The nitrogen primitive set is the (13s 8p 6d) set described in I; an uncontracted diffuse (1s 1p) set (exponents $\alpha_s = 0.056$, and $\alpha_p = 0.038$) is added in some calculations. The O primitive basis is that given in section IIIA above with the f functions omitted, and the H basis is also that of section IIIA, with the d functions omitted. The N_2 bond length is 2.074 a_0 and the H_2O geometry is that given in section IIIA above. SCF and SDCI energies were computed for applied fields of 0.005 a.u. (and the opposite sign where required by symmetry) and the polarizability components were determined by finite differences. The eight valence electrons were correlated in the H_2O calculations and the ten valence electrons in the N_2 calculations. In addition to the numerical second differentiation of the energy, we have evaluated polarizability components from the expectation value of the dipole operator over a wave function

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generated in the presence of a perturbing electric field. There is no reason for the two routes to agree for a truncated CI wave function, but in practice the values agreed to within 1% in all cases, so we report only the energy derivative values.

Table 6 lists computed polarizabilities for N_2. There is clearly a very considerable contraction error associated with the [5s 4p 3d] ANO set, but this is almost entirely alleviated by replacing the most weakly occupied d-type ANO by the outermost d primitive. This is especially true when a diffuse (1s 1p) set is added to the basis. Evidently these additional functions provide enough flexibility in the sp basis to make it unnecessary to replace the most weakly occupied ANOs by the outermost s and p primitives, as doing this after adding the diffuse set affects the computed polarizabilities by much less than 1% (although the contraction error actually increases slightly), and the results are very close to the uncontracted basis. On the other hand, if the diffuse set is not added the effect of uncontracting the outermost s and p primitives is 1-2%, and the results are still more than 1% from the uncontracted basis values, at least for α_{xx}. This behaviour has also been observed for CO by Bauschlicher and Barnes [20]. For the polarizability, therefore, it seems unnecessary to modify the ANO contraction in the sp space provided diffuse functions are added, although the loss in energy if the contraction is modified is hardly significant. If diffuse functions are not added the contraction must be modified by leaving the outermost functions uncontracted.

The H_2O polarizability results listed in Table 7 show similar behaviour to Ne and N_2. No diffuse functions were added in this case, and the inadequacy of the unmodified ANO contraction can be clearly seen in the SCF and SDCI polarizability values. The out-of-plane component α_{yy} shows

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a contraction error of more than 20%. On the other hand, replacing the most weakly occupied ANOs with the outermost primitives uncontracted essentially eliminates the contraction error, with little loss in energy. The modified contraction thus performs even better for H_2O than for N_2, and the molecular results thus strongly support the conclusions drawn in the previous subsection and elsewhere [4,5,20] about basis set contraction and polarizabilities.

IV. Conclusions.

The present study is both broader in scope and more detailed than our previous work [5], or various individual investigations that have appeared (see, for example, Ref. 6 and references therein). The major conclusions remain unchanged: while ANO contractions appear to give the best molecular energies obtainable with contracted sets of a given size, their performance on properties is equally good only for quantities that depend directly on the energy, such as spectroscopic constants. Of the one-electron properties we have studied, the "point" properties, such as EFGs, are also well described by unmodified ANO contractions, although the convergence of the contraction error in these properties seems slower than for the energy. Multipole moments and related properties like diamagnetic susceptibilities show unacceptably large contraction errors using even the largest unmodified ANO sets, and it is necessary to modify the contraction scheme to rectify this. Simply uncontracting the outermost primitive is all that is usually required, and for larger primitive sets this will be accompanied by a much smaller contraction loss in the energy than would be obtained with segmented contracted sets of the same size. Second-order properties such as polarizabilities have stringent demands on the primitive basis, requiring the addition of diffuse functions (possibly of high angular momentum), but it appears that the modified ANO contraction scheme can be used to generate compact contracted sets for these properties as well.

Acknowledgements

References

1. J. Almlöf and P. R. Taylor, *J. Chem. Phys.* **86**, 4070 (1987).
2. G. A. Petersson and M. Braunstein, *J. Chem. Phys.* **83**, 5129 (1985).
3. E. R. Davidson and D. Feller, *Chem. Rev.* **86**, 681 (1986).
4. C. W. Bauschlicher, *Chem. Phys. Lett.* **142**, 71 (1987).
5. J. Almlöf, T. Helgaker and P. R. Taylor, *J. Phys. Chem.* **92**, 3029 (1988).
6. C. W. Bauschlicher, S. R. Langhoff and P. R. Taylor, *Adv. Chem. Phys.*, in press.
7. T. H. Dunning, Jr, *J. Chem. Phys.* **90**, 1007 (1989).
8. C. W. Bauschlicher and P. R. Taylor, *Theor. Chim. Acta* **74**, 63 (1988).
9. MOLECULE-SWEDEN is an electronic structure program system written by J. Almlöf, C. W. Bauschlicher, M. R. A. Blomberg, D. P. Chong, A. Heiberg, S. R. Langhoff, P.-Å. Malmqvist, A. P. Rendell, B. O. Roos, P. E. M. Siegbahn, and P. R. Taylor.
10. G. Maroulis, M. Sana and G. Leroy, *Int. J. Quantum Chem.* **19**, 43 (1981).
11. F. B. van Duijneveldt, *IBM Research Report RJ 945* (IBM, San Jose, 1971).
12. R. D. Cowan and D. C. Griffin, *J. Opt. Soc. Am.* **66**, 1010 (1976); R. L. Martin, *J. Phys. Chem.* **87**, 750 (1983).
13. T. H. Dunning, Jr, *J. Chem. Phys.* **66**, 1382 (1977).
14. K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
15. R. C. Raffenetti, *J. Chem. Phys.* **58**, 4452 (1973).
16. S. R. Langhoff, C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.* **86**, 6992 (1987).
17. S. R. Langhoff, C. W. Bauschlicher and P. R. Taylor, *J. Chem. Phys.*, submitted for publication.
18. H.-J. Werner and W. Meyer, *Mol. Phys.* **31**, 855 (1976).
19. A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
20. C. W. Bauschlicher and L. A. Barnes, *Chem. Phys.* **124**, 383 (1988).
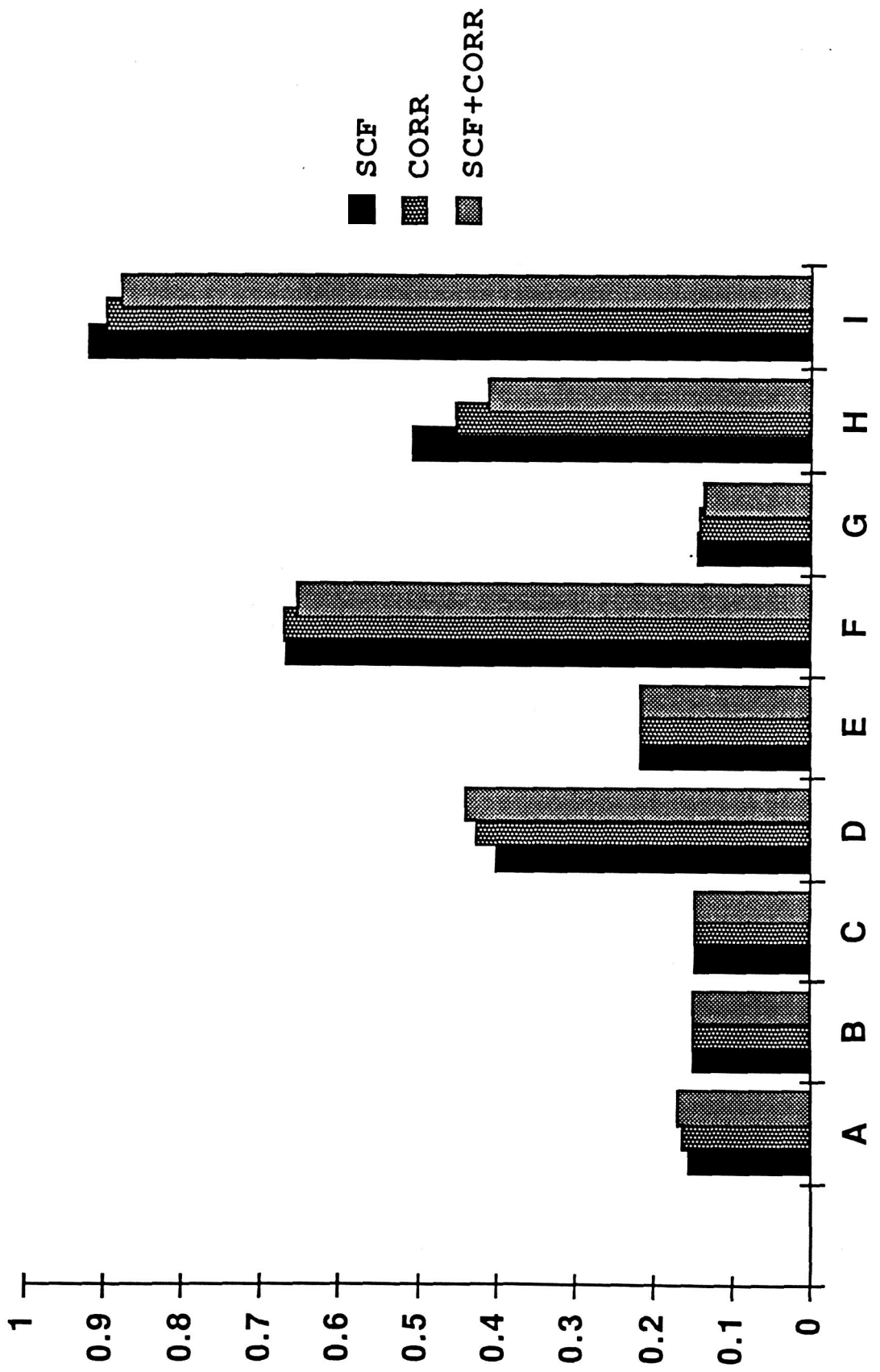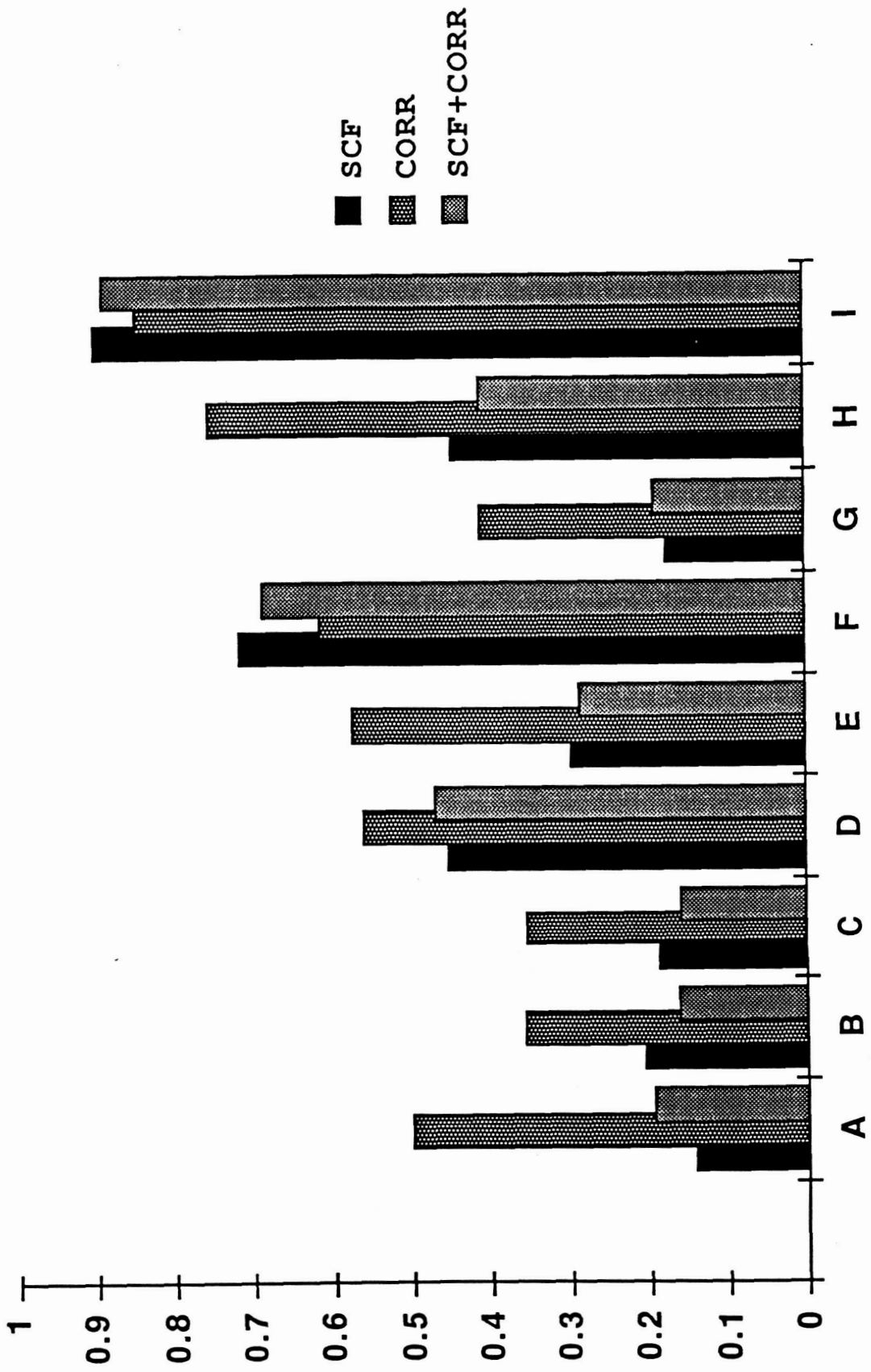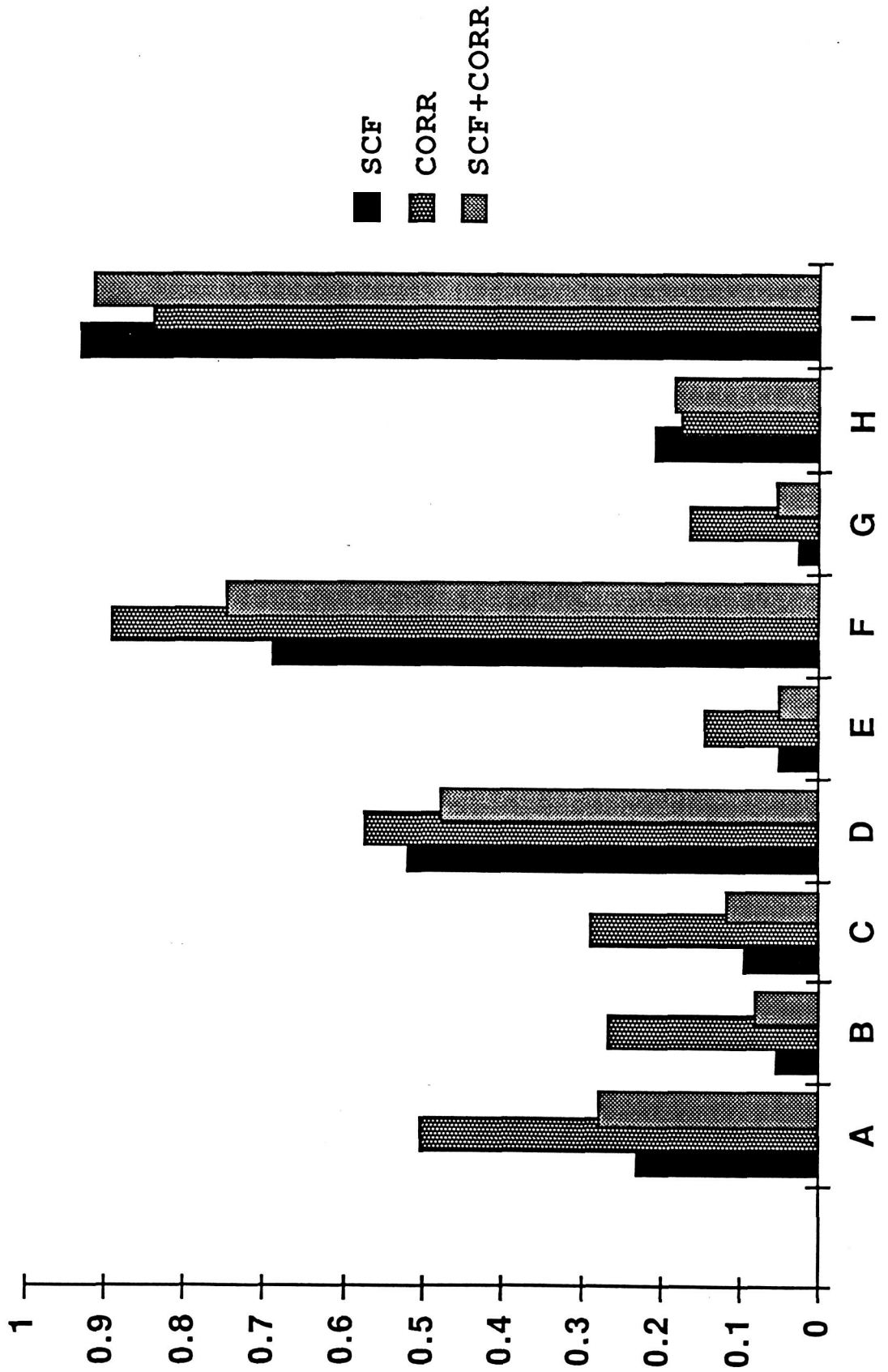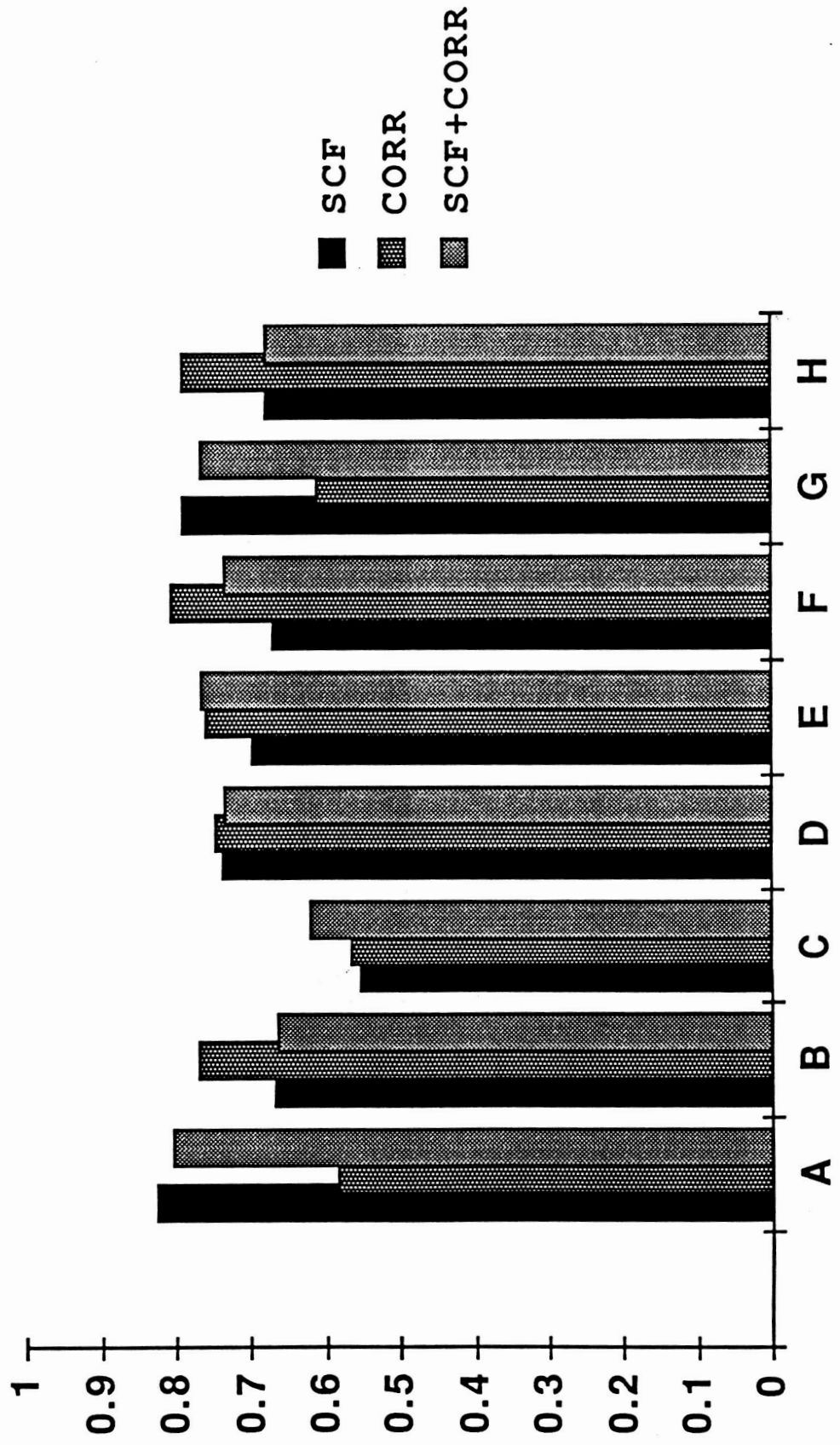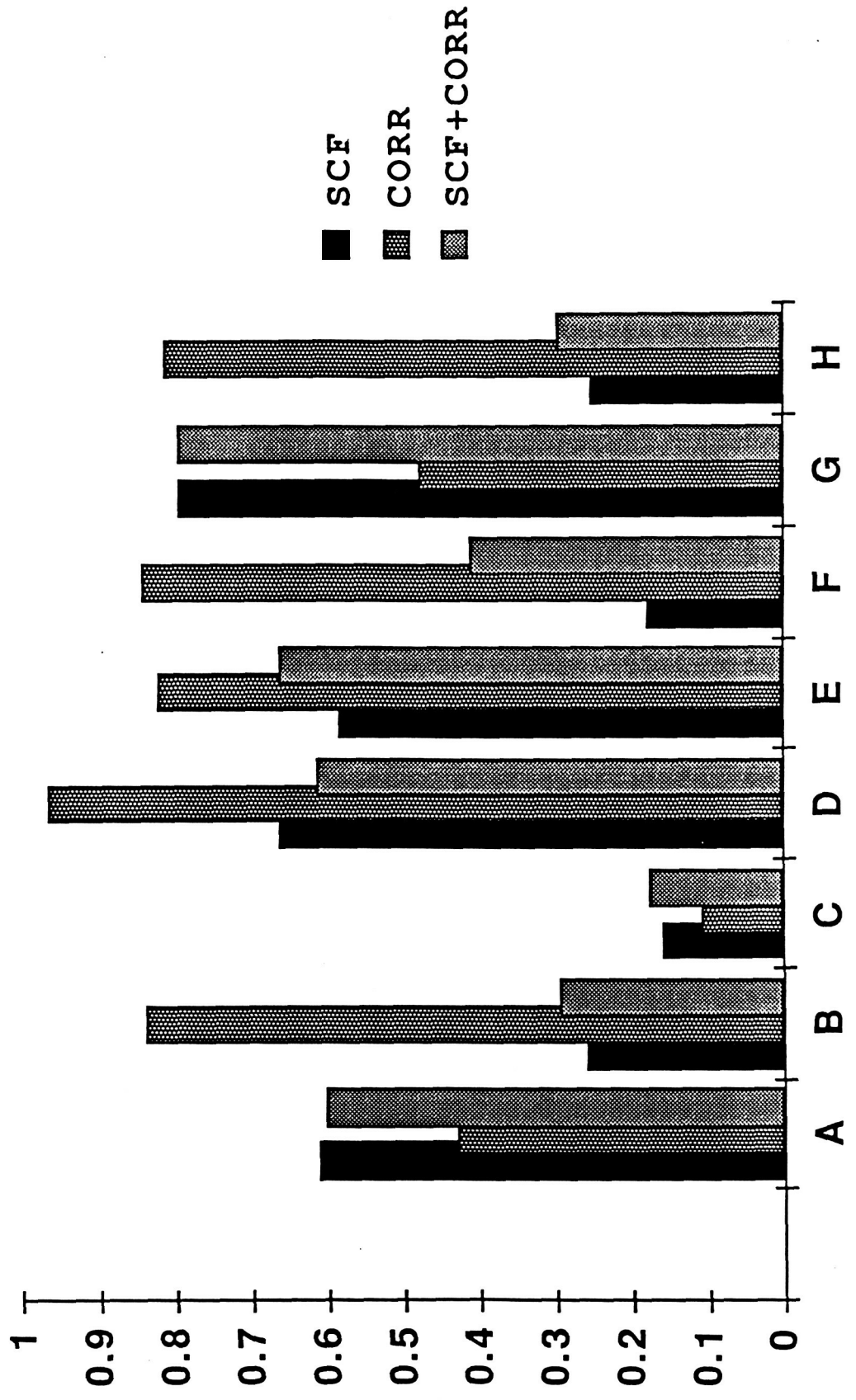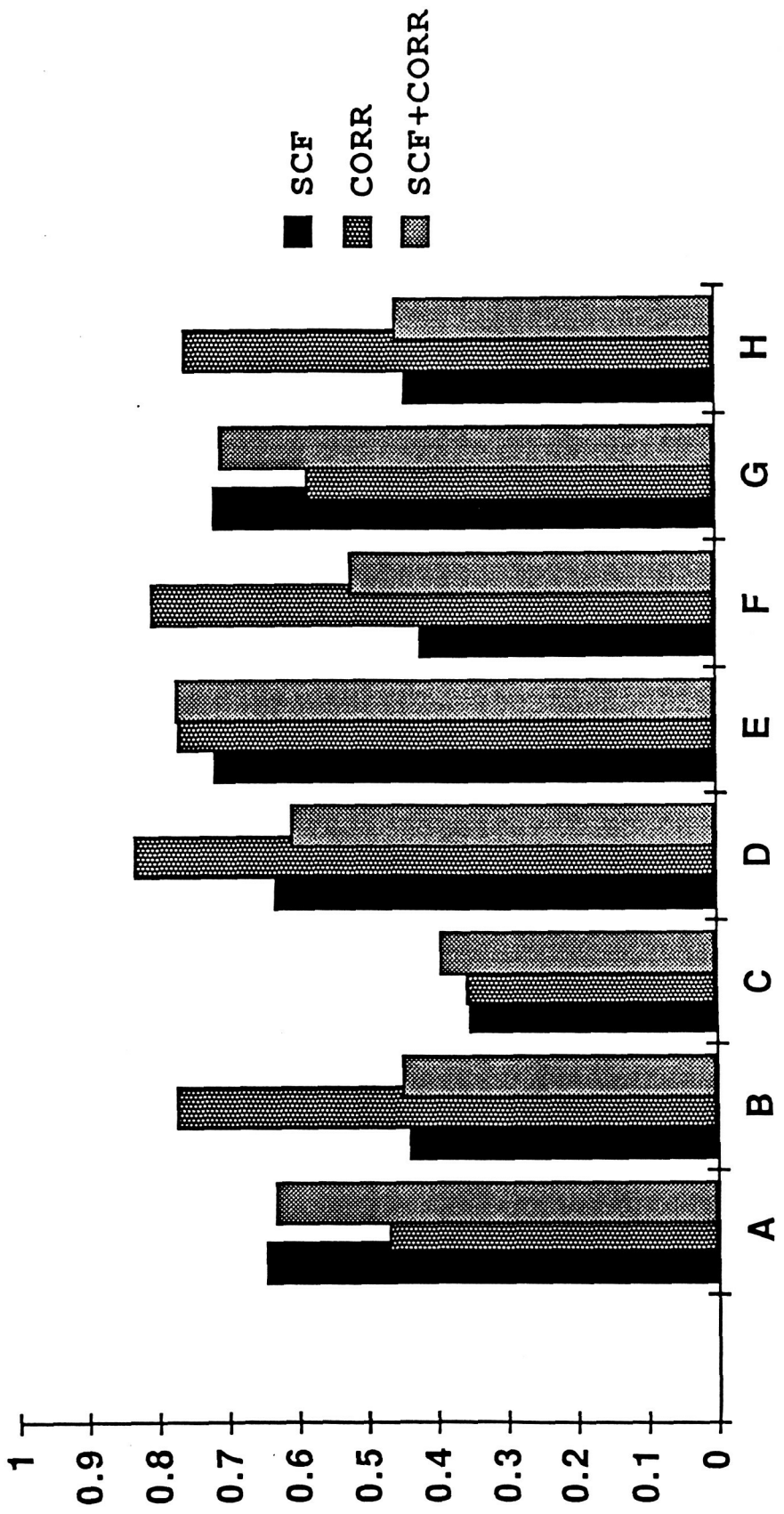
Table 1. H$_2$O SCF and SDCI point properties[a] (all values in atomic units). Entries for the uncontracted basis (U) show total values; for the contracted basis sets the contraction errors are given.

Basis set and designation	Energy	r^{-1} [b]	EFG O$_{xx}$	EFG O$_{yy}$	EFG H$_{xx}$	EFG H$_{yy}$	EFG H$_{xz}$
U (13s 8p 6d 4f/8s 6p 4d)	-76.067080	-0.0686	-1.6200	1.8021	-0.2265	0.2621	-0.3177
	-76.340323	-0.0587	-1.5057	1.6878	-0.2313	0.2658	-0.3234
A [5s 4p 3d 2f/4s 3p 2d]	0.000636	-0.0016	-0.0355	0.0350	-0.0028	0.0035	-0.0039
	0.003490	-0.0021	-0.0343	0.0342	-0.0031	0.0040	-0.0043
B [4+1s 3+1p 2+1d 2f/3+1s 2+1p 2d]	0.000572	-0.0006	-0.0456	0.0577	-0.0025	0.0015	-0.0020
	0.005150	-0.0004	-0.0420	0.0544	-0.0029	0.0020	-0.0027
C [4+1s 3+1p 2+1d 2f/3+1s 2+1p 2d] + (1s 1p 1d) on O	0.000392	-0.0003	-0.0455	0.0535	-0.0027	0.0021	-0.0028
	0.004864	0.0000	-0.0418	0.0501	-0.0031	0.0025	-0.0035
D [4s 3p 2d 1f/3s 2p 1d]	0.002508	-0.0042	-0.1415	0.1454	-0.0095	0.0101	-0.0158
	0.014127	-0.0054	-0.1538	0.1625	-0.0107	0.0114	-0.0178
E [3+1s 2+1p 2d 1f/2+1s 2p 1d]	0.001252	-0.0018	-0.0513	0.0516	-0.0075	0.0090	-0.0139
	0.023035	0.0001	-0.0329	0.0317	-0.0097	0.0113	-0.0172
F [3s 2p 1d/2s 1p]	0.008466	-0.0093	-0.0792	0.0978	-0.0276	0.0371	-0.0460
	0.064935	-0.0121	-0.0680	0.0914	-0.0293	0.0386	-0.0464
G [5s 4p 3d 2f/4s 3p 2d] segmented	0.005367	-0.0004	-0.0304	0.0292	-0.0062	0.0067	-0.0110
	0.016241	0.0006	-0.0238	0.0231	-0.0075	0.0081	-0.0131
H [4s 3p 2d 1f/3s 2p 1d] segmented	0.058075	-0.0059	-0.0649	0.0365	-0.0091	0.0095	-0.0152
	0.082060	-0.0041	-0.0301	-0.0039	-0.0115	0.0122	-0.0191
I [3s 2p 1d/2s 1p] segmented	0.069596	-0.0118	-0.0840	0.0679	-0.0448	0.0579	-0.0766
	0.129705	-0.0147	-0.0656	0.0551	-0.0469	0.0602	-0.0782

[a] Upper entries SCF, lower entries SDCI
[b] Potential at (0, 0, -2)

Table 2. H2O SCF and SDCI permanent moments[a] (all values in atomic units). Entries for the uncontracted basis (U) show total values; for the contracted basis sets the contraction errors are given.

Basis set and designation	μ	Θ_{xx}	Θ_{yy}	Ω_{xxz}	Ω_{yyz}	χ_{zz}
U (13s 8p 6d 4f/8s 6p 4d)	0.779200	1.7962	-1.8844	3.6718	-1.7313	-19.6933
	0.733700	1.8019	-1.8762	3.5781	-1.6971	-20.1785
A [5s 4p 3d 2f/4s 3p 2d]	0.008500	-0.0246	0.0215	-0.0507	0.0253	0.1073
	0.018000	-0.0307	0.0283	-0.0468	0.0352	0.2319
B [4+1s 3+1p 2+1d 2f/3+1s 2+1p 2d]	0.000200	-0.0032	-0.0001	-0.0161	0.0150	-0.0001
	0.005300	-0.0016	-0.0018	0.0029	0.0061	0.0587
C [4+1s 3+1p 2+1d 2f/3+1s 2+1p 2d] + (1s 1p 1d) on O	0.001800	0.0098	-0.0190	-0.0041	0.0042	-0.0385
	0.007300	0.0145	-0.0257	0.0165	-0.0057	0.0080
D [4s 3p 2d 1f/3s 2p 1d]	0.011200	-0.0676	0.0714	-0.1422	0.0728	0.1875
	0.019600	-0.0878	0.0947	-0.1635	0.0978	0.3474
E [3+1s 2+1p 2d 1f/2+1s 2p 1d]	0.003000	-0.0052	0.0010	-0.0110	0.0100	0.0063
	0.001800	-0.0038	-0.0015	-0.0062	0.0035	-0.0349
F [3s 2p 1d/2s 1p]	0.037100	-0.0750	0.0290	0.0328	-0.0607	0.2819
	0.040300	-0.1412	0.0986	-0.1249	0.0257	0.4865
G [5s 4p 3d 2f/4s 3p 2d] segmented	0.002900	0.0008	-0.0010	0.0054	0.0010	0.0006
	0.006800	0.0032	-0.0017	0.0225	-0.0073	0.0124
H [4s 3p 2d 1f/3s 2p 1d] segmented	0.029900	-0.0002	-0.0079	0.0304	-0.0149	0.0090
	0.030100	0.0014	-0.0112	0.0380	-0.0237	-0.0411
I [3s 2p 1d/2s 1p] segmented	0.052800	-0.1512	0.1217	-0.2076	0.1081	0.2960
	0.060900	-0.2097	0.1864	-0.3519	0.1961	0.4448

Upper entries SCF, lower entries SDCI

Table 3. HBr SCF and SDCI properties[a] (all values in atomic units). Entries for the uncontracted basis (U) show total values; for the contracted basis sets the contraction errors are given.

Basis	Energy[b]	ΔE_{rel}	Ω_{zz}	Θ_{zz}	μ_z	EFG Br$_{zz}$	EFG H$_{zz}$
U (14s 13p 7d 4f/8s 6p 4d)	-0.981707	-0.0701	4.3617	3.1823	0.3737	-7.0811	-0.2280
	-1.172431	-0.0699	4.4989	3.0460	0.3333	-6.8022	-0.2330
A ANO [7s 6p 4d 2f/4s 3p 2d]	0.000632	-0.0046	0.0586	0.0410	0.0008	0.3493	0.0021
	0.001846	-0.0046	0.0351	0.0428	0.0021	0.3535	0.0022
B ANO [6+1s 5+1p 3+1d 1+1f/3+1s 2+1p 1+1d]	0.000543	-0.0047	0.0388	0.0023	0.0015	0.4357	0.0006
	0.003989	-0.0048	0.0167	-0.0037	-0.0005	0.4384	-0.0004
C ANO [7+1s 6+1p 4+1d 2+1f/4+1s 3+1p 2+1d]	0.000229	-0.0043	0.0129	0.0026	0.0011	0.2611	0.0011
	0.000725	-0.0043	0.0121	0.0022	0.0009	0.2680	0.0018
D Raffenetti [7s 6p 4d 2f/4s 3p 2d] (H as ANOs)	0.001516	-0.0188	0.1111	0.0176	0.0033	0.3886	0.0004
	0.005552	-0.0189	0.0744	0.0110	0.0016	0.3962	0.0000
E segmented [7s 6p 4d 2f/4s 3p 2d]	0.696938	-1.3196	0.0133	0.0050	0.0006	-0.9068	-0.0009
	0.700999	-1.3197	-0.0058	0.0002	-0.0011	-0.8818	-0.0016
F Raffenetti [7s 6p 4d 2f/4s 3p 2d]	0.001361	-0.0188	0.0235	0.0053	0.0006	0.3755	-0.0005
	0.006324	-0.0189	0.0027	0.0006	-0.0011	0.3920	-0.0013
G ANO Br/Br– [7s 6p 4d 2f/4s 3p 2d]	0.000632	-0.0090	0.0768	0.0567	0.0018	0.4671	0.0015
	0.002260	-0.0087	0.0507	0.0583	0.0025	0.4675	0.0015
H ANO Br/Br– [6+1s 5+1p 3+1d 1+1f/3+1s 2+1p 1+1d]	0.000536	-0.0072	0.0385	0.0028	0.0014	0.5109	0.0006
	0.004132	-0.0072	0.0164	-0.0027	-0.0003	0.5150	-0.0005

[a] Upper entries SCF, lower entries SDCI

[b] Energy+2572 E_h

Table 4. OH MRCI spectroscopic constants[a] and dipole moment[b]

Basis	r_e	D_e	ω_e	μ_{max}	r^{μ}_{max}
(13s 8p 6d 4f/8s 6p 4d) + (1s 1p)	0.970	4.58	3706	0.6681	2.275
[5s 4p 3+1d 2f/4s 3p 2d] + (1s 1p)	0.971	4.57	3708	0.6689	2.283
[4+1s 3+1p 3+1d 2f/4s 3p 2d] + (1s 1p)	0.970	4.58	3710	0.6678	2.281
[5s 4p 3d 2f/4s 3p 2d]	c	c	c	0.6779	2.265

[a] r_e in Å, D_e in eV, ω_e in cm^{-1}

[b] r^{μ}_{max} in a_0, μ_{max} in a.u.

[c] Not computed

Table 5. Ne SCF and SDCI polarizabilities[a] (a.u.)

Basis	Energy	α	γ	B	C
(13s 8p 6d 4f) + (2s 2p 1d 1f)	-128.546582	2.376	69.27	-13.24	3.12
	-128.832599	2.601	98.50	-16.57	3.46
[4+1s 3+1p 2+1d 1+1f] + (2s 2p 1d 1f)	-128.546578	2.339	69.58	-13.37	3.10
	-128.821244	2.570	97.62	-16.79	3.46
[5s 4p 3d 2f] + (2s 2p 1d 1f)	-128.546551	2.155	80.02	-12.67	3.00
	-128.828787	2.345	113.70	-16.18	3.34
[4s 3p 2d 1f] + (2s 2p 1d 1f)	-128.546502	1.962	84.71	-12.43	2.86
	-128.816958	2.137	122.48	-16.20	3.23
[5s 4p 3d 2f] + (2s 2p 1d 1f) segmented	-128.537378	2.371	68.61	-13.17	3.11
	-128.800440	2.616	98.23	-16.75	3.49
[4s 3p 2d 1f] + (2s 2p 1d 1f) segmented	-128.484156	2.223	67.85	-13.28	3.02
	-128.712219	2.487	100.90	-17.25	3.44

[a] Upper entries SCF, lower entries SDCI

Table 6. N$_2$ SCF and SDCI polarizability[a] (a.u.)

Basis	Energy	α_{xx}	α_{zz}
(13s 8p 6d) + (1s 1p)	-108.98960710	9.83	14.99
	-109.32584703	9.94	14.70
[5s 4p 3d] + (1s 1p)	-108.98841523	9.17	14.92
	-109.32219279	9.33	14.60
[5s 4p 2+1d] + (1s 1p)	-108.98835063	9.74	15.00
	-109.32022835	9.84	14.70
[4+1s 3+1p 2+1d] + (1s 1p)	-108.98766491	9.70	14.95
	-109.31813476	9.82	14.64
(13s 8p 6d)	-108.98958719	9.81	14.97
	-109.32579458	9.92	14.62
[5s 4p 3d]	-108.98805099	8.81	14.64
	-109.32150923	8.93	14.20
[5s 4p 2+1d]	-108.98803587	9.55	14.74
	-109.31967725	9.63	14.30
[4+1s 3+1p 2+1d]	-108.98764123	9.65	14.93
	-109.31783766	9.78	14.60

[a] Upper entries SCF, lower entries SDCI

Table 7. H_2O SCF and SDCI dipole moment and polarizability[a] (a.u.)

Basis	Energy	μ	α_{xx}	α_{yy}	α_{zz}
(13s 8p 6d/8s 6p)	-76.065465	0.780	9.17	7.81	8.43
	-76.313308	0.738	9.68	8.69	9.10
[4+1s 3+1p 2+1d/3+1s 2+1p]	-76.064621	0.780	9.14	7.78	8.38
	-76.307892	0.739	9.62	8.67	9.04
[5s 4p 3d/4s 3p]	-76.064749	0.788	8.62	6.12	7.63
	-76.310205	0.751	8.93	6.52	8.07

[a] Upper entries SCF, lower entries SDCI