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The dissociation energy of N_2

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Abstract

We examine the requirements for very accurate *ab initio* quantum chemical prediction of dissociation energies using a detailed investigation of the nitrogen molecule. Although agreement with experiment to within 1 kcal/mol is not achieved even with the most elaborate multireference CI wave functions and largest basis sets currently feasible, it is possible to obtain agreement to within about 2 kcal/mol, or 1% of the dissociation energy. At this level it is necessary to account for core-valence correlation effects and to include up to *h*-type functions in the basis. We have also investigated the effect of *i*-type functions, the use of different reference configuration spaces, and basis set superposition error. After discussing these results, we speculate on the remaining sources of error in our best calculations.

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I. Introduction

The dissociation energy (D_e) of the nitrogen molecule has often been used as a test of the capabilities of quantum chemical methods. The experimental value of 228.4 kcal/mol [1] is larger than most diatomic D_e values, and there is a very large correlation contribution, with the SCF result being little more than half that of experiment. An accurate computed D_e value thus requires a very sophisticated treatment of the correlation problem. (Our discussion here excludes calculations in which good agreement with experiment derives from cancellations of errors or from basis set superposition error). In a recent study using an elaborate multireference CI (MRCI) wave function and a basis set with up to g-type functions, Langhoff, Bauschlicher and Taylor (LBT) [2] obtained a D_e value of 224 kcal/mol. This is the same as the value obtained by Binkley and Frisch [3] using an MP4 treatment of correlation and a smaller basis set: the comparison of single-reference results given by Ahlrichs and co-workers [4] (who obtained 214 kcal/mol using the coupled-pair functional approach and a basis set somewhat smaller than Ref. 2) suggests that MP4 probably overestimates D_e. However, the LBT result is itself actually an overestimate, by some 2.5 kcal/mol, because the deletion of σ virtual orbitals necessitated by near linear dependence degrades the asymptotic description by this amount. Further, correction for basis set superposition error would reduce the LBT result by almost 0.5 kcal/mol, and the D_e value of Binkley and Frisch by almost 3 kcal/mol. Hence the best *ab initio* estimate so far, in the sense of degree of correlation treatment and size and saturation of basis set, is around 221 kcal/mol.

An error of 7.5 kcal/mol in a D_e value of 228.4 kcal/mol is not a large relative error, but it is considerably larger than the commonly-stated target of "chemical accuracy" (1 kcal/mol). If the inadequacies of quantum chemical methodology are to be understood, it would be desirable to investigate how the N_2 ground-state D_e value can be computed to higher accuracy. A number of possible sources of error can be considered. First, the correlation treatment could be inadequate. This might involve either inadequacies in the MRCI reference space, or the lack of size-consistency in the CI expansion. Further, the LBT results were obtained from a treatment in which the core electrons were not correlated, and the core correlation results of Ahlrichs *et al.* [4] suggest that this could account for almost 1 kcal/mol. Second, the basis set used by LBT includes up to g-type functions: there may thus be errors from neglect of higher angular functions. There may also be errors from lack of saturation of the primitive or contracted sets used. Third, the question of basis set superposition error, which may give a spurious increase in D_e, should be investigated. Finally, we may note here that relativistic effects, as estimated by first-order perturbation theory [5], contribute less than 0.1 kcal/mol to the binding (actually decreasing D_e very slightly). They can be neglected for our present purposes. Spin-orbit effects should be negligible for the N_2 ground-state dissociation as all the atomic 2*p* orbitals participate in the bonding. It also seems reasonable to assume that other effects such as Born-Oppenheimer breakdown terms can also be neglected.

In the present work we shall discuss in detail all of the above potential sources of error. A brief description of the computational methods is given in the next section, but it will be more convenient to discuss the details of wave functions and basis sets in the later sections. In Section III we consider the effects of extending the correlation treatment, including the effects of core-valence correlation and the question of size-consistency. The effect of improving the basis set, including both extending the primitive and contracted *s*, *p*, *d*, *f*, and *g* spaces and adding *h*- and *i*-type functions, is described in Section IV, together with the question of basis set superposition error. Our best theoretical estimates of D_e and other spectroscopic constants, together with possible sources of remaining errors, are discussed in Section V, and our conclusions are given in Section VI.

II. Computational methods.

The basis sets used in the present calculations are derived from two different primitive Gaussian basis sets: a (13*s* 8*p* 6*d* 4*f* 2*g*) set and a larger (18*s* 13*p* 6*d* 5*f* 4*g* 3*h* 2*i*) set. The latter should be close to saturation in all l values included. The *sp* sets are from van Duijneveldt [6] and Partridge [7], respectively. The polarization sets are even-tempered with a ratio of 2.5 between successive exponents; these are based on geometric mean exponents of $(1.2)^{l-2}$. The primitive sets were contracted using atomic natural orbitals [8] for the N (^4S) ground state. The various contracted sets used are described in Sections III and IV.

The molecular orbitals used were obtained from CASSCF wave functions in which the 2*p*-derived orbitals and electrons were active, giving six active electrons in six orbitals in the CASSCF calculations. The use of orbitals from a larger active space CASSCF calculation, in which all ten valence electrons are active in the eight valence orbitals, was investigated, but near r_e the two active spaces yield almost the same orbitals, while at large internuclear distances the larger active space creates difficulties in defining the orbitals for a subsequent CI calculation because of $1s/2s$ orbital mixing. We therefore report here only results obtained with molecular orbitals from the smaller CASSCF active space.

All MRCI wave functions used in this work are based on CAS reference spaces, that is, all configuration state functions (CSFs) that can be generated with a particular choice of active space are used as references. Two active spaces have been used, one in which six electrons are distributed among six active orbitals, nominally derived from the atom $2p$ orbitals, and a larger space in which all ten valence electrons are distributed among the eight valence orbitals. The calculations are labelled MRCI(6act) and MRCI(10act), respectively. It should be noted that ten electrons are correlated in all MRCI wave functions, the difference arises from whether the $2s$ electrons and orbitals are included in the active space or not. In addition to the MRCI results, we also quote results obtained using a multireference analog [9] of Davidson's correction [10], and with the averaged coupled-pair functional (ACPF) method of Gdanitz and Ahlrichs [11].

Spectroscopic constants (r_e, ω_e, and D_e) were obtained by fitting computed energy points to a polynomial in $1/r$, as described in detail in Section V below. The use of $1/r$ rather than r as the independent variable provides a more rapidly convergent expansion of the potential energy about a given point [12]. For the investigation of changes in basis sets and correlation treatment the "dissociation energy" was computed as the difference between the total energy at 2.1 a_0 (close to the experimental equilibrium) and 100 a_0. Tests show that the differential effects associated with a change in the level of treatment would not be affected by the use of another (similar) r value.

All calculations were performed using the MOLECULE–SWEDEN [13,14] program system on the CRAY X–MP/48 and NAS Facility CRAY Y–MP/832 at NASA Ames and the CRAY-2 at the Minnesota Supercomputer Center.

III. Convergence of D_e with correlation treatment.

The D_e values obtained from different correlation treatments in a [$5s$ $4p$ $3d$ $2f$ $1g$] basis (contracted from the smaller primitive set) are listed in Table 1. The MRCI(6act) calculations correspond to those of LBT, although as noted in the introduction their result was somewhat larger because of an unbalanced treatment of the atoms relative to the molecule. The close agreement between the MRCI(6act)+Q and ACPF(6act) results suggest that the multireference Davidson correction for higher excitations gives reliable results here. The D_e value obtained from the MRCI(10act) calculation is very similar to that from MRCI(6act)+Q (or ACPF(6act)), but the effect of the +Q correction (or of ACPF) on the MRCI(10act) calculation is to *decrease* D_e, which is somewhat unexpected. The different behavior with the different MRCI reference spaces can be understood by examining their performance on the states of nitrogen atom.

Table 2 lists total energies for the lowest states of nitrogen atom (derived from the occupation $2s^2 2p^3$) and separations between them. The separation between the two lowest states, ^4S and ^2D, is not affected by the change from an SCF-based description (singles and doubles CI (SDCI) equivalent to a three active orbital CASSCF reference or to the 6act treatment of N_2) to an MRCI based on a five-electron four active orbital CASSCF treatment (equivalent to the 10act treatment of N_2), because only one CSF of the appropriate symmetry can be formed in this active space in the atom. This is not the case for the $^4S - {}^2P$ separation, as the CASSCF treatment for the atom accounts for $2s/2p$ near-degeneracy mixing in the ^2P state. As the $^4S - {}^2P$ separation is overestimated by the 6act treatment of N_2, the mixing of configurations derived from the $^2P + {}^2P$ limit into the molecular wave function will be underestimated, reducing the strength of the bond and underestimating D_e. Hence it is reasonable that the MRCI(10act) treatment produces a larger D_e than MRCI(6act). Incidentally, the discrepancies between the best calculated atomic term separations given in Table 2 and the experimental values [15] are entirely due to basis set deficiencies: the use of a $[6s\ 5p\ 4d\ 3f\ 2g\ 1h\ 1i]$ ANO basis reduces the separations by about 0.04 eV at the correlated level, bringing them into almost perfect agreement with experiment.

The rather unexpected reduction in D_e on going from the MRCI(10act) treatment to MRCI(10act)+Q can also be understood in terms of N atom. The most important correlating configuration in the ^4S ground state is the single orbital excitation $2s \rightarrow 3d$, accompanied by a recoupling of the $2p$ electrons. This is essentially a purely atomic effect, as we have noted before [2]. For the MRCI(6act) calculation at infinite separation this excitation can occur on only one of the atoms at a time, because of the spin and symmetry coupling constraints on the reference CSFs.

However, in the MRCI(10act) calculation this effect can occur on both atoms at the same time because there are far fewer coupling restrictions on the active occupations compared to the MRCI(6act) case. The possibility of recovering more atomic correlation at the MRCI(10act) level results in a *reduction* in the weight of the reference CSFs in the MRCI(10act) wave function relative to MRCI(6act), at infinite separation, while near r_e the larger active space calculation has an increased weight of the reference CSFs relative to MRCI(6act). Of course, as the larger calculation allows important atomic correlation effects on both atoms simultaneously it can legitimately be regarded as more size-consistent than MRCI(6act), and so inclusion of the +Q correction results in double counting some effects. We conclude that while the MRCI(6act)+Q results are to be preferred over MRCI(6act), the uncorrected MRCI(10act) results should be more reliable than MRCI(10act)+Q.

An effect excluded from the calculations discussed so far is core correlation. In CPF calculations in which all 14 electrons were correlated, Ahlrichs and co-workers obtained a increase of some 0.7 kcal/mol in D_e as a result of core correlation [4]. Experience suggests that the core-core correlation will be unimportant and that this effect represents core-valence correlation. We have computed the effect of core-valence correlation on D_e by performing multireference CI calculations based on MRCI(6act), but with additional CSFs in which one electron is excited from the core orbitals together with one (or none) from the valence orbitals. The basis set used for these calculations comprised the uncontracted (13*s* 8*p* 6*d*) set described above, augmented with the *f* ANO with the largest occupation number from the smaller ANO set. Tests on core-valence correlation in nitrogen atom demonstrated that higher-exponent *d* functions or other higher angular momentum functions made a negligible contribution. The core-valence contribution to D_e was computed to be 0.7 kcal/mol, in remarkable agreement with the work of Ahlrichs *et al* [4]. From the lack of sensitivity of the atomic core-valence correlation to changes in basis set or correlation treatment it can safely be concluded that the D_e value of N_2 is increased by less than 1 kcal/mol as a result of core-valence correlation.

IV. Convergence of D_e with basis set.

Table 3 shows the variation in the D_e value of N_2 with atomic basis set. These results were obtained at the MRCI(6act) level. (The difference between MRCI(10act) and MRCI(6act) was explored for several different basis sets, but was found to be the same (0.7 kcal/mol in D_e) for all the large basis sets.) We consider first the effect of expanding the contracted set obtained from the (13*s* 8*p* 6*d* 4*f* 2*g*) primitive set. The extension from [4*s* 3*p* 2*d* 1*f*] to [5*s* 4*p* 3*d* 2*f*] and then to [6*s* 5*p* 4*d* 3*f*] indicates that the contraction error in D_e in the latter basis should be less than 0.5 kcal/mol. Adding a diffuse *sp* set increases D_e by only 0.2 kcal/mol. Comparing the [5*s* 4*p* 3*d* 2*f* 1*g*] and [5*s* 4*p* 3*d* 2*f*] results shows that the *g* ANO increases D_e by 2.5 kcal/mol: this is a little smaller than the 3.0 kcal/mol observed by Ahlrichs *et al* [4], but the smaller primitive sets used in Ref. 4 may lead to effects which are actually due to *d* and *f* set unsaturation being attributed to the *g* set. Adding *spdfg* ANOs to the [5*s* 4*p* 3*d* 2*f* 1*g*] set increases D_e by 1.5 kcal/mol: comparing this number with the 1.2 kcal/mol observed on adding *spdf* ANOs to the [5*s* 4*p* 3*d* 2*f*] set suggests that additional *g* orbitals would increase D_e by only 0.3 kcal/mol. Finally, adding a single *h* primitive set to the [6*s* 5*p* 4*d* 3*f* 2*g*] basis increases D_e by 0.7 kcal/mol, suggesting that the total contribution of *h* and higher angular momentum functions will be on the borderline of "chemical accuracy".

The effect of replacing the (13*s* 8*p* 6*d* 4*f* 2*g*) primitive set with the (18*s* 13*p* 6*d* 5*f* 4*g*) primitive set is to increase D_e by only 0.1 kcal/mol in a [5*s* 4*p* 3*d* 2*f* 1*g*] contracted set. Thus the smaller primitive set seems to be saturated in all the angular momentum quantum numbers, at least as far as the D_e value is concerned. Adding an *h*-type ANO, contracted from 3 primitive functions, increases D_e by 1.1 kcal/mol, but this is actually an overestimate of the *h* effect, as there is partial compensation for unsaturation of the *spdfg* space. When the *h* ANO is added to the [6*s* 5*p* 4*d* 3*f* 2*g*] ANO set the increase in D_e is 0.8 kcal/mol, only slightly more than the effect of the single *h* primitive, and consistent with the effect of increasing the contracted set from [5*s* 4*p* 3*d* 2*f* 1*g* 1*h*] to [6*s* 5*p* 4*d* 3*f* 2*g* 1*h*]. This gives an increase in D_e of 1.1 kcal/mol. Finally, the addition of an *i*-type ANO, contracted from two primitive *i* functions, increases D_e by 0.4 kcal/mol. It therefore seems safe to conclude that the contribution to D_e from higher than *i*-type functions will be less than 0.3 kcal/mol.

The need to include *g*- and *h*-type functions in the basis set to achieve chemical accuracy in the N_2 D_e value creates rather large basis sets. It is useful to examine the contributions of the different components of the angular sets, in case some are noticeably more important than others. If this is the case, the basis set could be reduced by eliminating the unimportant components, with a consequent reduction in the overall computational effort. This possibility has been investigated by computing the contribution to D_e made by the f, g and h components in the [5s 4p 3d 2f 1g 1h] basis (using the small primitive set for the f and g investigations and the large set for the h case). Various approaches were tried, such as selectively deleting each angular component or adding only the desired angular component, but all gave essentially the same results. Table 4 displays the increase in D_e obtained with successive addition of different components. First, it appears that there is little scope for reducing the basis set, as the differences between the contribution from different angular components is seldom large. Further, the main contribution in the f case is to the π and δ spaces, while in the g case this shifts to the δ and ϕ spaces. This is perhaps surprising: it seems plausible to expect the g_γ functions to be the most important when g functions are first added, for instance, as they are the first functions of γ type to be included. However, this is not what is observed. It is also clear the the contribution of higher angular functions becomes more "isotropic" as the angular quantum number increases, as the h example in Table 4 shows. This effect becomes more pronounced on noting that in the case of π or higher components two members of a degenerate pair of orbitals are added together. Overall, then, it must be concluded that it is necessary to include all members of any set of higher angular functions that are added.

The last aspect of our basis set investigations is the question of basis set superposition error (BSSE). In the smaller primitive basis the BSSE contribution to D_e (that is, twice the energy lowering obtained by including a ghost basis in an atom calculation) is computed to be 0.28 kcal/mol in the [6s 5p 4d 3f 2g 1h] contracted set, to be compared with 0.36 and 0.73 kcal/mol in the [6s 5p 4d 3f 2g] and [6s 5p 4d 3f] sets, respectively. This is determined using a counterpoise correction with the full ghost basis. Thus in our largest calculations BSSE should not exceed 0.3 kcal/mol.

V. Computed spectroscopic constants.

Table 5 contains our best directly computed results for D_e, ω_e, and r_e. These results are obtained from a sixth-order fit in $1/r$ to eleven points around equilibrium, obtained from MRCI(6act) calculations in a [6s 5p 4d 3f 2g 1h] contracted basis (large primitive set). The agreement with the experimentally derived values for r_e and ω_e is very good, but the computed D_e value is still 3.2 kcal/mol less than the experimental value. From the results presented in the preceding sections we can add 0.7 kcal/mol to our computed value to account for core-valence correlation, add 0.4 kcal/mol for the effect of adding an *i*-type function, and subtract 0.3 kcal/mol for the effects of BSSE. Thus based on the various calculations presented above we obtain an estimate of 226.0 kcal/mol, which is still outside chemical accuracy in terms of agreement with experiment, but is accurate to essentially 1% of D_e.

We may speculate on the remaining sources of error in the theoretical D_e value. By extrapolating from the basis set investigations of Section IV it seems very likely that additional *spdfghi* functions would add at most 0.5 kcal/mol to D_e, and the contribution of higher than *i*-type functions can hardly exceed 0.3 kcal/mol. These effects would reduce the discrepancy to 1.6 kcal/mol. It seems unlikely that additional core or core-valence correlation could give rise to an effect of this magnitude, and it is highly improbable that more exotic phenomena, such as Born-Oppenheimer breakdown or the diagonal Born-Oppenheimer correction, could contribute to even within an order of magnitude. Relativistic effects have also been shown to be negligible, as discussed above. It therefore seems likely that the valence correlation treatment is still in error by 1.6 kcal/mol. This is not inconsistent with the molecular consequences of quite subtle changes in the description of the atomic limits, as discussed in Section III above. The best way to resolve this question would be to perform 10-electron full CI calculations on N_2, using a realistic basis set such as the valence double zeta plus polarization set used by Bauschlicher and Langhoff [16]. Recent advances in the computational methodology of full CI calculations [17,18] should make such a calculation possible in the near future.

VI. Conclusions.

Even with very elaborate MRCI wave functions and extended ANO basis sets with high angular momentum functions, it is not yet possible to compute the dissociation energy of N_2 from first priniciples to within 1 kcal/mol — a somewhat arbitrary definition of chemical accuracy. However, an accuracy of about 1% does appear to be achievable. From the results of this work it appears safe to assert that the basis set limit for a calculation using the MRCI(6act) configuration space and including Davidson's correction for higher excitations is a D_e value of 226.8 kcal/mol. The remaining 1.6 kcal/mol difference with experiment is most probably attributable to inadequacies in the valence correlation treatment, suggesting that larger reference spaces will be required.

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Table 1. Convergence of N_2 D_e (kcal/mol) with correlation treatment[a].

Method	6 active electrons	10 active electrons
Reference[b]	204.5	211.9
MRCI	222.1	222.8
MRCI+Q	222.6	221.6
ACPF	222.5	221.5
Ref. weight[c] (2.1 a_0)	93.7	94.2
Ref. weight (100 a_0)	93.3	93.0

[a] [5*s* 4*p* 3*d* 2*f* 1*g*] ANO basis.

[b] Energy obtained with reference CSFs.

[c] Weight of reference CSFs in MRCI wave function (percentage) at stated r(NN).

Table 2. N atom term separations (eV)[a].

Method	$^4S - ^2D$	$^4S - ^2P$
SCF	2.85	4.71
SDCI	2.45	3.72
SDCI+Q	2.42	3.58
CASSCF[b]		3.77
MRCI		3.65
MRCI+Q		3.64
Expt[c]	2.38	3.58

[a] [5*s* 4*p* 3*d* 2*f* 1*g*] ANO basis.

[b] 5 active electrons in 4 active orbitals. This reduces to an SCF wave function for the ^4S and ^2D states.

[c] Moore, Ref. 14.

Table 3. Convergence of D_e (kcal/mol) with atomic basis set[a].

Basis set	D_e
	(13s 8p 6d 4f 2g 1h) primitive set
[4s 3p 2d 1f]	216.0
[5s 4p 3d 2f]	219.6
[6s 5p 4d 3f]	220.8
[6s 5p 4d 3f]+ diffuse sp	221.0
[5s 4p 3d 2f 1g]	222.1
[6s 5p 4d 3f 2g]	223.6
[6s 5p 4d 3f 2g 1h]	224.3
	(18s 13p 6d 5f 4g 3h 2i) primitive set
[5s 4p 3d 2f 1g]	222.3
[5s 4p 3d 2f 1g 1h]	223.4
[5s 4p 3d 2f 1g 1h 1i]	224.0
[6s 5p 4d 3f 2g]	223.7
[6s 5p 4d 3f 2g 1h]	224.5
[6s 5p 4d 3f 2g 1h 1i]	225.0

[a] MRCI(6act) calculation

[b] See text for details of primitive basis sets.

Table 4. D_e contributions (kcal/mol) from different angular components[a].

Component	$2f$ set	$1g$ set	$1h$ set
σ	0.81	0.19	0.10
π	2.98	0.57	0.11
δ	3.08	0.72	0.16
ϕ	1.39	0.71	0.20
γ		0.32	0.15
η			0.06

[a] MRCI(6act) calculation; small primitive basis for *f* and *g* case,added to a [5*s* 4*p* 3*d*] ANO set. Large primitive basis for *h* case, added to a [6*s* 5*p* 4*d*] ANO set.

Table 5. Spectroscopic constants for N_2[a].

	r_e(Å)	ω_e (cm^{-1})	D_e(kcal/mol)
Computed	1.100	2353	225.2
Experiment[b]	1.098	2359	228.4

[a] MRCI(6act)+Q calculation; [6*s* 5*p* 4*d* 3*f* 2*g* 1*h*] ANO basis (large primitive set).

[b] Huber and Herzberg, Ref. 1.