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Ab initio Calculations on NO_2 and NO_2^-: Optimization of Diffuse Gaussian Exponents*

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Ab initio calculations of NO_2 and NO_2^-, using a Dunning [4*s*3*p*] basis augmented by 1 component diffuse *s* and *p* functions were carried out. The SCF energies of NO_2 and NO_2^- (ground states) as a function of O_s, O_p, N_s, and N_p diffuse function exponents are given and discussed. The curves show some unexpected features which make the optimization of the diffuse function exponents problematic.

The SCF vertical electron detachment energy for NO_2^- as a function of the diffuse O_s, O_p, N_s, and N_p exponents is then discussed. Except for the case of O_p, the detachment energy is essentially independent of the O_s, N_s, and N_p exponents. Finally, results of SCF and MCSCF/CI calculations of the electron affinity of NO_2 are given and compared with experiment.

Key words: NO_2^- electron detachment energy – Basis set optimization

1. Introduction

In carrying out *ab initio* calculations of molecular properties which use Gaussian basis sets, the problem arises regarding how to adjust the basis set for the molecular species under consideration. A procedure often used is to scale the exponents. That is, the exponents of the functions in the basis set are optimized by calculations on atoms [1, 2] or small molecules [3, 4]. Then they are corrected for the appropriate molecular environment by multiplying the exponents of all the basis functions of

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a given type by a common scaling factor [2–4] which is chosen to optimize the computed energy.

For calculations involving negative ions, it is desirable to add diffuse *s* and *p* functions to a standard basis set and then the problem of exponent choice arises. In this case one method would be to use the optimum exponents as determined from the negative atom ions (if available) and scale them to the molecular ion environment. If the added diffuse functions are one component *s* and *p* functions, then the above method is equivalent to a direct exponent optimization of the diffuse functions in the molecular ion environment.

A main purpose of this note is to point out that there can be problems with this method of optimization. In particular, SCF calculations were carried out on NO_2 and NO_2^- using the Dunning [4*s*3*p*] contraction [5] of the (9*s*5*p*) Huzinaga [1] basis set augmented by one-component diffuse Gaussian *s* and *p* functions on each atom center. Attempts at optimization of the exponents of the diffuse *s* and *p* functions gives, in several cases, meaningless energy minima or no minima at all. Only in the case of diffuse oxygen *p* functions on NO_2^- is a meaningful minimum obtained.

The above raises the question whether all the diffuse N and O *s* and *p* functions are necessary, or a smaller set will suffice. Because of computation time considerations, such a question is important if one wishes to add polarization functions to the basis set. It is seen that, from the standpoint of energy lowering, all the functions, except possibly the N_p function, are necessary with O_p giving the most lowering, followed in order by O_s, N_s, and N_p. (O_s and O_p refers to diffuse *s* and *p* functions on both oxygen atoms.) However, for the vertical NO_2^- electron detachment energy, which is an energy difference, the O_p and either the O_s or the N_s functions are sufficient. This result differs from that of Andersen and Simons [6] who found, using a Dunning [4*s*2*p*] basis, that augmentation by diffuse in-plane O_p functions and N_s and N_p functions were all necessary.

As a partial check on the appropriateness of the most diffuse components of the Huzinaga (9*s*5*p*) basis for NO_2, the exponents of the most diffuse N_s, N_p, O_s, and O_p components were separately reoptimized for NO_2, while keeping the [4*s*3*p*] contraction fixed. The new exponents were all 3%–10% smaller than the original values. Use of these reoptimized exponents in the basis gave an NO_2^- SCF energy lowering of 0.002 hartree over the original SCF [4*s*3*p*] value. Since this is 10% of the lowering obtained by augmentation, one concludes that augmentation of the [4*s*3*p*] basis is necessary and that not much is to be gained by reoptimizing the Huzinaga basis.

Finally, results of MCSCF and MCSCF/CI calculations using the augmented [4*s*3*p*] basis set, of both the vertical e^- detachment energy of NO_2^- and the NO_2 electron affinity are given. The very good agreement between theory and experiment for the electron affinity at the SCF level disappears at the MCSCF and MCSCF/CI levels.

2. Calculation

All the calculations reported on here use the Dunning [4*s*3*p*] contraction of the Huzinaga (9*s*5*p*) basis. For many of the results, this basis was augmented by 1 component diffuse *s*- and *p*-functions centered on the N and O atoms. Unless explicitly stated otherwise, the N_p and O_p diffuse exponents were taken to be [7] 0.048 and 0.059, respectively (optimum values for N^- and O^- ions) with the *s* exponents arbitrarily chosen equal to the corresponding atom *p* exponents.

The calculations were done either at the NO_2^- equilibrium geometry [8] $d_{N-O} = d_{N-O'} = 2.3356$ bohrs and $\angle ONO' = 115.4°$ or at the NO_2 equilibrium geometry [9] $d_{N-O} = d_{N-O'} = 2.2552$ bohrs and $\angle ONO' = 134.1°$. Most of the calculations reported on here are SCF calculations. For the MCSCF and MCSCF/CI [10] calculations the configuration space consisted of all single and double plus selected triple and quadruple excitations into the valence space from the HF configuration. The N_{1s}, O_{1s}, and O_{2s} orbitals were held as core orbitals with excitations from the N_{2s} orbital [11] (and all the *p* orbitals) allowed. The CI configuration list contained all single and double excitations from those reference configurations with coefficient magnitudes $\geqslant 0.1$ in a CI calculation [12][1]. The MCSCF configuration list contained all spin components of those spatial configurations which had one or more spin components with coefficient magnitudes $\geqslant 0.03$ in the CI calculations. The MCSCF calculations (which gave as output, orbitals to be used as input to a CI calculation) and CI calculations were repeated, making changes in the MCSCF and CI configuration lists to comply with the above acceptance criteria, until the lists were stable.

3. Results

Since there is no reason why diffuse function exponents which are optimum for negative N and O ions should be optimum for molecules containing N and O, calculations were made in which the diffuse N and O *s* and *p* exponents were each varied one at a time with the remaining 3 diffuse function exponents held at their canonical values mentioned before. Figs. 1 and 2 show the results of SCF calculations on $NO_2(X^2A_1)$ and $NO_2^-(X^1A_1)$, all made at the NO_2^- experimental equilibrium ground-state C_{2v} geometry [8] of $d_{N-O} = 2.3356$ bohrs and an ONO angle of 115.4°. The abcissa shows the exponent variation and the ordinate, the energy. The results of variation of the O_s and O_p exponents on NO_2 and NO_2^- are given in Figs. 1 (NO_2) and 1 (NO_2^-). The results of variation of the N_s and N_p exponents for NO_2 and NO_2^- are given in Figs. 2 (NO_2) and 2 (NO_2^-), respectively. The O_s and O_p curves give the results for simultaneous changes in both O atoms in NO_2 and in NO_2^-. The arrows on the abscissae locate the smallest O_s, O_p, N_s, and N_p exponents in the [4*s*3*p*] Dunning set. The circles and triangles all represent the calculated points which are connected by smooth curves.

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[1] The Batelle Ohio State CI program of Sharitt and coworkers as adopted by J. Rosenberg was used. See Ref. [12].

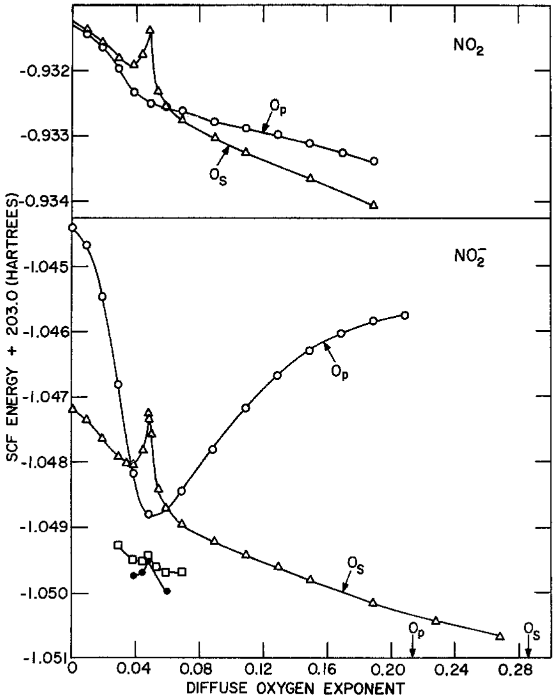

Fig. 1. SCF energy for the NO_2 and NO_2^- ground state at the NO_2^- equilibrium geometry as a function of the diffuse O_s and O_p function exponents. Fig. 1 (NO_2) gives the energies for NO_2 and Fig. 1 (NO_2^-) gives the energies for NO_2^-. For each curve the non-varying exponents of the diffuse functions were fixed at the values of $N_s = N_p = 0.048$, and for the O_s curves $O_p = 0.059$ and for the O_p curves $O_s = 0.059$. The points marked with circles (O_p), triangles (O_s), squares, and solid circles are the actual computed SCF values. They are connected by the smooth curves. The curve marked with squares is an O_s curve for NO_2^- but with the N_s diffuse exponent set equal to 0.168 instead of 0.048. The curve marked with solid circles is an O_s curve for NO_2^- with a *two* component diffuse N_s Gaussian with N_s exponents equal to 0.048 and 0.168

The curves show quite a diversity in shape. The N_s and O_s curves for both NO_2^- and NO_2 show a general energy lowering as the *s* exponent is increased, with the exception of a sharp peak which is quite sharp and narrow in the case of the O_s curves. The O_p curve for NO_2 and the N_p curves for NO_2 and NO_2^- show a similar energy lowering as the *p* exponent is increased without the presence of a sharp peak. The O_p curve for NO_2^- is unique in showing a (relatively) deep minimum with no energy lowering as the exponent is increased.

The intersection of the curves with the ordinate, which correspond to zero values of the diffuse Gaussian exponent are the SCF energy values which one gets if one removes the corresponding diffuse Gaussian component from the basis set. For example, the O_s curve for NO_2^- intersects the ordinate at an energy of -204.0472 hartrees. This is also the SCF energy for NO_2^- with 1 component diffuse *p* functions on the N and O atoms and a 1 component diffuse *s* function on the N atom only. The ordinate intersections for the other curves have corresponding interpretations. This clearly follows from the fact that a basis function component with a very small exponent is spread over a large region of space and thus has a very small overlap with functions which are concentrated around the atom centers. In each case the curves descend initially as one moves away from the origin. This shows that adding in diffuse N_s or N_p or O_s or O_p components with small exponents to the basis, even in the presence of the remaining 3 diffuse component function types, lowers the SCF energy.

In seeking for an explanation of the peaks in the N_s and O_s curves, it is noted that,

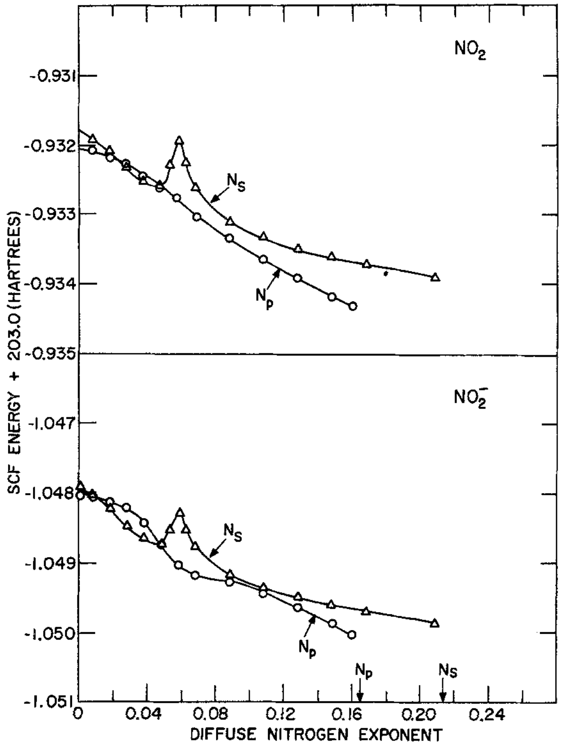

Fig. 2. SCF energy for the NO_2 and NO_2^- ground state at the NO_2^- equilibrium geometry as a function of the diffuse N_s and N_p exponents. The description, given for Fig. 1 with N_s replacing O_s and N_p replacing O_p and without the solid circles and squares, applies here

as one varies the exponent through the peak regions, the relative sign of the most diffuse *s* function in the [4*s*3*p*] set and the added *s* function changes for each SCF orbital.

For example, let $\phi_D^{O_s}$ be the most diffuse *s* type Gaussian for oxygen in the [4*s*3*p*] set, and let $\phi_a^{O_s}$ be the added *s* type diffuse Gaussian. The SCF calculations give each orbital in terms of optimized expansion coefficients for the Gaussian basis. Thus a general orbital can be written as $\cdots + c(\alpha)\phi_D^{O_s} + d(\alpha)\phi_a^{O_s}(\alpha) + \cdots$ where the coefficients $c(\alpha)$ and $d(\alpha)$, which can be either positive or negative, have the dependence on the added-function Gaussian exponent α made explicit. The dots refer to the other components in the expansion. Changing the relative sign of an orbital component as one goes from α_1 to α_2 means that one goes from

$$\cdots|c(\alpha_1)|\phi_D^{O_s}+|d(\alpha_1)|\phi_a^{O_s}(\alpha_1)\cdots \quad \text{to} \quad \cdots|c(\alpha_2)|\phi_D^{O_s}-|d(\alpha_2)|\phi_a^{O_s}(\alpha_2)\cdots$$

or from

$$\cdots|c(\alpha_1)|\phi_D^{O_s}-|d(\alpha_1)|\phi_a^{O_s}(\alpha_1)\cdots \quad \text{to} \quad \cdots|c(\alpha_1)|\phi_D^{O_s}+|d(\alpha_2)|\phi_a^{O_s}(\alpha_2)\cdots$$

where $|-|$ denotes the absolute value. The remaining two possibilities are obtained by multiplying each of the above by -1.

Now suppose for some orbital the first possibility given above represents the change. This means that $d(\alpha_1)$ is positive and $d(\alpha_2)$ is negative. By the argument of continuity (the coefficients of the components in the orbitals must be continuous functions of the exponents), there must be some exponent value α' between α_1 and α_2 for which $d(\alpha')=0$. But $d(\alpha')=0$ means that the energy contribution at α' of this orbital is the same as if no diffuse oxygen *s* components were present at all. (Because of C_{2v} symmetry the magnitudes and *relative* signs of $c(\alpha)$ and $d(\alpha)$ must be the same on both oxygen atoms.)

Suppose now that the SCF orbitals were such that the diffuse oxygen *s* component coefficients had a value of zero at the same value of α' for all orbitals. By the previous argument the SCF energy at this value becomes equal to the SCF energy computed without any diffuse oxygen *s* component in the basis set, i.e., the energy value at the intersection of the O_s curve with the ordinate. It is thus clear that in this case a sharp spike should exist at α' in the O_s SCF energy curve with a peak value equal to the ordinate intersection value.

One can, in this case, regard the O_s SCF energy curve as two curves which join one another at the spike. For values of $\alpha<\alpha'$ one has an SCF energy curve with orbitals each of which has a fixed relative sign between the $\phi_D^{O_s}$ and $\phi_a^{O_s}$ coefficients. That is, for each SCF orbital the value of $c(\alpha)d(\alpha)/|c(\alpha)d(\alpha)|$ (either $+1$ or -1) is independent of α for $\alpha\leqslant\alpha'$. Of course, the value of $c(\alpha)d(\alpha)/|c(\alpha)d(\alpha)|$ need not be the same for each orbital. For values of $\alpha\geqslant\alpha'$ one has another SCF energy curve with relative sign values for each orbital opposite to those of the above curve. These two curves join at $\alpha=\alpha'$ where $c(\alpha')d(\alpha')/|c(\alpha')d(\alpha')|=0/0$.

The actual situation for the N_s and O_s curves for NO_2 and NO_2^- is very close to this. For each of these 4 cases, the relative signs of the $\phi_D^{N_s}$ and $\phi_a^{N_s}$ components and the $\phi_D^{O_s}$ and $\phi_a^{O_s}$ components respectively for each orbital changes over a very small region of exponent variation of -0.003 to 0.01. Thus, on this basis one would predict, from an examination of the SCF orbital changes with the diffuse *s* exponents, the existence of such a spike for each of the 4 cases.

It is unclear at present why the relative signs of the $\phi_D^{O_s}$ and $\phi_a^{O_s}$ coefficients for all the SCF orbitals should change around the same diffuse exponent value and similarly for $\phi_D^{N_s}$ and $\phi_a^{N_s}$. It should be noted that the value of α' corresponding to the peak in the O_s curves is the value (0.048) of the N_s diffuse exponent. Similarly, the value of α' corresponding to the peak in the N_s curves is the value (0.059) of the O_s diffuse exponents. At these points the diffuse *s* functions are identical on all three atom centers. Thus at these points the diffuse *s* function parts of the basis set have a symmetry which is higher than C_{2v}.

For the N_p and O_p curves there are as many relative sign changes for the $\phi_D^{N_p}$ and $\phi_a^{N_p}$ orbital components as there are for the *s* orbital components. However, for each SCF orbital these changes occur for different exponent values. Also, within each orbital the relative sign changes for the p_z, p_y, and p_x components of the diffuse function often occur at different diffuse *p* function exponent values. Thus the N_p and O_p curves would not be expected to have the narrow peaks as do the O_s and N_s curves and, in fact, they do not, as inspection of Figs. 1 and 2 shows.

It should be noted that these sharp peaks in the N_s and O_s curves are not real physical effects in that they can be moved around or removed by changing exponents or functions in the diffuse basis. For example, if one sets the N_s diffuse exponent at 0.168 and varies the O_s diffuse exponent over the peak region for NO_2^-, the peak is essentially gone (curve with squares, Fig. 1). If one adds to the complete one-component diffuse component set an extra N_s function with exponent at 0.168, the peak is mostly gone (curve with solid circles Fig. 1).

Another general feature of the curves is that, with the exception of the NO_2^- O_p curve and the peaks, they all show an energy lowering as the diffuse exponent is increased. A study of the SCF orbitals $\cdots + c(\alpha)\phi_D^s + d(\alpha)\phi_a^s(\alpha) \cdots$ shows that as α is increased towards β, the smallest s component exponent in the [4*s*3*p*] basis on the atom being considered, $|c(\alpha)|$ and $|d(\alpha)|$ both become large but $c(\alpha)/|c(\alpha)| = -d(\alpha)/|d(\alpha)|$. Plots of $c(\alpha)\phi_D^s + d(\alpha)\phi_a^s(\alpha)$ for different orbitals give a variety of curves – some with nodes and some without. This suggests strongly that the reason for the SCF energy decrease as α increases is due to the increased flexibility of the basis set. If α is comparable to β then by suitable choice of $c(\alpha)$ and $d(\alpha)$ some orbitals can include *ns* character with $n > 2$. Other choices can in effect convert $c(\alpha)\phi_D^s + d(\alpha)\phi_a$ into a single component where the effective exponent then can be different for different orbitals. It is also clear that for small values of α, $c(\alpha)\phi_D + d(\alpha)\phi_a(\alpha)$ is effectively just ϕ_D over the important space regions as $\phi_a(\alpha) \rightarrow$ constant as $\alpha \rightarrow 0$.

The energy lowering in NO_2^- due to the addition of diffuse functions to the [4*s*3*p*] basis, as well as the shape of the curves in Figs. 1 and 2, suggests that the smallest exponents of the Dunning [4*s*3*p*] basis set itself may not be optimum for NO_2^-. To this end SCF calculations without the diffuse functions in the basis were made at the NO_2^- equilibrium geometry where the smallest O_s, O_p, N_s, and N_p exponents in the [4*s*3*p*] set were separately varied to find the energy minimum (a harmonic variation of the energy in the neighborhood of the minimum was assumed).

Table 1 gives the results. Column 2 gives the value [1] of the smallest exponent for each of the four types and column 3 gives the values found here for NO_2^-. It is seen that optimization of the most diffuse [4*s*3*p*] exponents for NO_2^- decreases their values by 0.005 to 0.022. While this suggests a more diffuse [4*s*3*p*] basis may be appropriate for NO_2^-, this change is not large considering the fact that NO_2^- is a negative ion and the exponents in the (9*s*5*p*) primitive basis [1] were optimized on atoms. This is borne out by noting that the NO_2^- SCF energy, calculated with the

Table 1. Optimization for NO_2^- of most diffuse part of Dunning [4*s*3*p*] basis exponent

Type	Dunning	Optimized
N_s	0.2133	0.1908
N_p	0.1654	0.1601
O_s	0.2846	0.2731
O_p	0.2137	0.2008
SCF energy (hartrees)	−204.02748	−204.02990

most diffuse part of the [4*s*3*p*] basis reoptimized gives an energy of -204.02991 hartrees which is only 0.068 eV (0.0025 hartree) below the original [4*s*3*p*] value (last row of Table 1). Since the augmented [4*s*3*p*] SCF energy for NO_2^- is -204.04873, it is clear that adding 1 component diffuse functions to the [4*s*3*p*] basis is much more important for NO_2^- than is optimizing the exponents of the most diffuse components of the [4*s*3*p*] set. Addition of diffuse functions to the [4*s*3*p*} basis is less important for NO_2. SCF calculations for NO_2 at its experimental equilibrium geometry [9] give [4*s*3*p*] and augmented [4*s*3*p*] values of -203.95605 and -203.96243 hartrees, respectively. This gives an energy difference of 0.0064 hartree which is about 1/3 the corresponding energy difference 0.0213 hartree for NO_2^-.

It is clear from Figs. 1 and 2 that attempts to optimize the diffuse component exponents by minimizing the SCF energy in either NO_2 or NO_2^- will not work in general. Except for O_p in NO_2^-, one either gets a false minimum just to the left of the peaks in the *s* curves or no minimum at all in the case of the N_p and NO_2O_p curves. This suggests that one should optimize the diffuse exponents by use [6] of the vertical e^- detachment energy of NO_2^- which is the difference between appropriate pairs of curves in Figs. 1 and 2.

Fig. 3 shows the NO_2^- vertical e^- detachment energy as a function of the diffuse exponent for N_s, O_s, N_p, O_p obtained from the NO_2 and NO_2^- results given in Figs. 1 and 2. In the case of N_s, N_p, and O_s, the e^- detachment energy curves are almost flat (for N_p the total e^- detachment energy change over the range of exponent change is 0.0006 hartrees for N_p and even less for O_s and N_s. On the other hand, the O_p curve shows a strong e^- detachment energy dependence on the O_p diffuse exponent.

One concludes from the curves of Fig. 3 that even in the presence of N_s, O_s, and N_p diffuse components in the basis, the O_p diffuse component contributes to the e^- detachment energy. Also, the peak in the N_s and O_s functions of Figs. 1 and 2 is not present – thus whatever is the ultimate cause of the peaks, it has essentially no effect on the e^- detachment energy. Finally, the independence of the e^- detachment energy for N_p, N_s, and O_s on the corresponding diffuse exponents, plus the fact that all three curves give essentially the same detachment energy at zero exponent, means that the effect on the detachment energy by any one of the three function types (N_p, N_s, or O_s) is accounted for by the remaining two$+O_p$. For example, adding an N_s diffuse function to the [4*s*3*p*]+diffuse $O_p+O_s+N_p$ basis set does not affect the e^- detachment energy. Similarly, the addition of O_s diffuse functions [one for each O atom] to the [4*s*3*p*]+diffuse $O_p+N_s+N_p$ basis set does not affect the e^- detachment energy. A similar remark holds for N_p.

Note that this does not mean that the N_s, O_s, and N_p diffuse components do not contribute to the e^- detachment energy. To see this and to find out which of the diffuse function types are necessary, SCF calculations were made with the following basis sets: [4*s*3*p*]$+O_p$ diffuse, [4*s*3*p*]$+(O_p+N_p)$ diffuse, [4*s*3*p*]$+(O_p+O_s)$ diffuse, and [4*s*3*p*]$+(O_p+N_s)$ diffuse. Table 2 presents the results. The first column gives the basis set and the second the exponents of the diffuse functions.

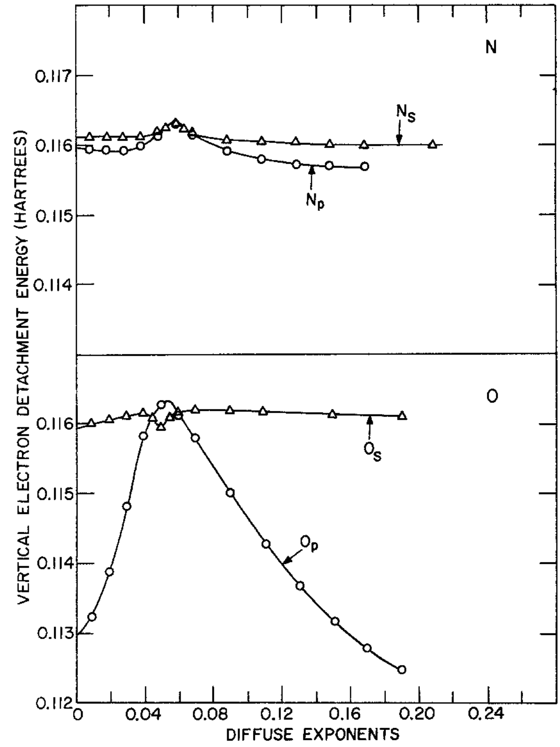

Fig. 3. SCF vertical electron detachment energy for NO_2^- as a function of the diffuse function exponent. The curves marked O_s, O_p, N_s, and N_p represent the difference of the corresponding O_s, O_p, N_s, and N_p curves of Figs. 1 and 2

(The O_p value is very close to the optimum value of 0.054, Figs. 1 and 3, and the N_p, N_s, and O_s values are the canonical ones.) The third and fourth columns give the corresponding NO_2 and NO_2^- SCF energy and the fifth and sixth columns give the NO_2^- vertical e^- detachment energy in hartrees and electron volts.

From Table 2 one sees that addition of one-component *s* and *p* diffuse functions to the [4*s*3*p*] basis drops the vertical e^- detachment energy from 2.76 eV to 3.16 eV or by 0.40 eV. Addition of a diffuse O_p component alone to the [4*s*3*p*] basis accounts for 0.22 eV or 55% of the 0.4 eV drop. Addition of the N_p diffuse function

Table 2. NO_2^- SCF vertical e^- detachment energy

Basis set	Diffuse exponents		Energy + 203.0 (hartrees) NO_2	NO_2^-	e^- Detachment energy hartrees	eV
[4*s*3*p*] —	—	—	−0.92607	−1.02748	0.10141	2.76
[4*s*3*p*] + O_p	O_p = 0.049		−0.92779	−1.03722	0.10942	2.98
[4*s*3*p*] + O_p + N_p	O_p = 0.049	N_p = 0.048	−0.92852	−1.03831	0.10978	2.99
[4*s*3*p*] + O_p + N_s	O_p = 0.049	N_s = 0.048	−0.93074	−1.04625	0.11550	3.14
[4*s*3*p*] + O_p + O_s	O_p = 0.049	O_s = 0.059	−0.93156	−1.04694	0.11538	3.14
[4*s*3*p*] + O_p + O_s + N_p + N_s	O_p = 0.049 N_s = N_p = 0.048	O_s = 0.059	−0.93249	−1.04879	0.11629	3.16

to the $[4s3p]+O_p$ basis has no effect. Addition of either the N_s or the O_s functions to the $[4s3p]+O_p$ basis account for an additional 41% of the lowering. Thus, use of either the O_p+O_s or the O_p+N_s diffuse components with the $[4s3p]$ basis accounts for 96% of the full augmented $[4s3p]$ energy lowering and thus suggests that for these purposes the full basis is unnecessary.

These results differ from those of Andersen and Simons [6] in that they found, using a $[4s2p]$ basis that, N_s, N_p and (in-plane-only) O_p diffuse components were necessary. With this augmented $[4s2p]$ basis they found a vertical e^- detachment energy of 2.66 eV instead of 3.16 eV as reported here. These differences probably result from the fact that a $[4s3p]$ basis was used here and the NO_2 energies were calculated from SCF NO_2^- energies by the EOM method in [6].

It is of interest to calculate the NO_2^-–NO_2 energy difference at their respective experimental equilibrium geometries. The reason is that this is essentially equal to the adiabatic electron affinity of NO_2. (Zero point vibrational corrections are expected to be small as they are equal to the difference in the zero point vibrational energies of NO_2 and NO_2^- in their respective ground states.)

There are many determinations of the NO_2 electron affinity in the literature [13–15]. Possibly the best values are those given by Hughes *et al.* [13] (which contain a list of some of the other literature values) 2.28 ± 0.1 eV, Duncan *et al.* [14], 2.38 ± 0.06 eV, and Herbst *et al.* [15], 2.36 ± 0.1 eV.

SCF calculations using both the $[4s3p]$ basis and the augmented $[4s3p]$ basis with N_s and N_p exponents equal to 0.048 and O_s and O_p exponents equal to 0.059 were carried out for both $NO_2^-(X^1A_1)$ and $NO_2(X^2A_1)$ at their respective equilibrium geometries. They gave values of 1.94 eV and 2.35 eV for the respective $[4s3p]$ and augmented $[4s3p]$ basis.

The remarkable agreement between the augmented SCF value and experiment must be regarded as fortuitous as SCF calculations neglect correlation effects. Andersen and Simons [6], using the EOM method on an SCF potential curve for NO_2^-, calculate an electron affinity of 2.25 eV. To further test the importance of correlation effects, MCSCF and MCSCF/CI calculations (described in Sect. 2) were carried out here on the augmented $[4s3p]$ basis with the previously given values of the N_s, N_p, O_s, and O_p diffuse exponents. The final calculations gave equilibrium geometry ground state NO_2 and NO_2^- energies of -204.15831 and -204.19417 hartrees which gives an NO_2 electron affinity of 0.98 eV. The difference between this value and the SCF value of 2.35 eV show the importance of molecular correlations to the NO_2 electron affinity. The difference between this value and the experimental values suggest the importance of either including *d* functions into the basis set or not neglecting excitations into the virtual space. Preliminary calculations suggest that inclusion of *d* functions will not reduce the discrepancy – thus correlation effects resulting from virtual space excitations must be the main source of the disagreement. The good agreement between the SCF value and experiment suggests that the correlation effects due to excitations into the valence space roughly cancel the remaining effects from excitations into the virtual space. However, this will have to await further calculations.

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References

1. Huzinaga, S.: J. Chem. Phys. **42**, 1293 (1965)
2. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971); Kari, R. E., Mezey, P. G., Csizmadia, I. G.: J. Chem. Phys. **63**, 581 (1975); **64**, 632 (1976)
3. Dunning, T. H., Jr.: J. Chem. Phys. **55**, 3958 (1971)
4. Goddard, J. D., Csizmadia, I. G., Mezey, P. G., Kari, R. E.: J. Chem. Phys. **66**, 3545 (1977)
5. Dunning, T. H., Jr.: J. Chem. Phys. **53**, 2823 (1970)
6. Andersen, E., Simons, J.: J. Chem. Phys. **66**, 2427 (1976)
7. Dunning, T. H., Jr., Hay, P. J.: Gaussian basis sets for molecular calculations, in: Methods of electronic structure theory, Schaefer, H. F. III Ed., pp. 1–27. New York: Plenum Publishing Corp. 1973
8. Sutton, L. E.: Tables of interatomic distances and configurations in molecules and ions, p. M47. Special Publication #11, The Chemical Society London 1958
9. Herzberg, G.: Electron spectra of polyatomic molecules, p. 602. Princeton, New Jersey: Van Nostrand 1966
10. Das, G., Wahl, A. C.: J. Chem. Phys. **56**, 1769 (1972); A bison MC Fortran computing system for calculations on atoms, diatoms, and polyatoms. ANL Report 7955 (1972)
11. Gillespie, G. D., Khan, A. U., Wahl, A. C., Hosteny, R. P., Krauss, M.: J. Chem. Phys. **63**, 3425 (1975)
12. Rosenberg, B. J.: PhD thesis, Ohio State University 1974
13. Hughes, B. M., Lifschitz, C., Tiernan, T. O.: J. Chem. Phys. **59**, 3162 (1973)
14. Dunkin, D. B., Fehsenfeld, F. C., Ferguson, E. E.: Chem. Phys. Letters **15**, 257 (1972)
15. Herbst, E., Patterson, T. A., Lineberger, W. G.: J. Chem. Phys. **61**, 1300 (1974)

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