Theor Chim Acta (1990) 77: 323–331

Theoretica Chimica Acta

Theoretical study of the $^6\Sigma^+$, $^6\Pi$, and $^4\Sigma^+$ van der Waals states of NO

Harry Partridge, Charles W. Bauschlicher, Jr., and Stephen R. Langhoff
NASA Ames Research Center, Moffett Field, CA 94035, USA

Received February 26, 1990/Accepted April 25, 1990

Summary. Potential energy curves for the weakly bound $^6\Sigma^+$, $^6\Pi$, and $^4\Sigma^+$ states of NO are presented at various levels of correlation treatment. The binding energies for the van der Waals minima vary from about 30 cm^{-1} for the $^6\Sigma^+$ state to about 20 cm^{-1} for the $^4\Sigma^+$ and $^6\Pi$ states. We investigate the importance of constraining the wave function to dissociate to a spherically symmetric O atom where the oxygen $2p$ orbitals are equivalent. For high levels of correlation treatment, we find that these restrictions have little effect on the potential, while greatly increasing the length of the CI expansion.

Key words: NO – van der Waals states – Equivalence restrictions – High-spin potentials

1. Introduction

The $^6\Pi$, $^6\Sigma^+$ and $^4\Sigma^+$ states of NO, which dissociate to ground-state atoms, are repulsive except for weak van der Waals minima. These states have not been observed spectroscopically and very limited attention has been given to them in *ab initio* calculations. Yet these high-spin potentials contribute substantially to transport properties such as the mobility, entropy and diffusion coefficients of hot ionized air, and their contribution to the transport properties (as measured by the collision integrals) is about 65% of the total N–O interaction [1]. Knowledge of these transport properties is important for modeling the chemistry occurring in the shock wave ahead of a reentering space vehicle.

Ab initio calculations of weakly bound systems are very difficult, because errors associated with many approximate methods are of the same order of magnitude as the well depth. Thus empirical approaches [2] have been used based on well-known atomic properties to estimate the potentials. For many van der Waals systems, the repulsive part of the potential can be approximated by an exponential term determined from the self-consistent field (SCF) potential. The full potential energy curves can then be estimated by adding this repulsive exponential term to an attractive dispersion term with a damping function. However, these empirical potentials are, in general, only qualitative, as even the functional form of such interactions is not well defined. The situation is simpler at long range where the charge densities of the systems do not overlap appreciably, exchange and overlap repulsions may be neglected, and the electrostatic and dispersion parameters may be derived from properties of the separated systems. This approach is particularly convenient for extending potential energy curves near the dissociation limit [3].

The van der Waals interaction energy at large r can be expressed in the form

$$-V_{LR}(r) = \frac{C_6}{r^6} + \frac{C_8}{r^8} + \cdots$$

where C_6 is the dispersion coefficient corresponding to the induced dipole-induced dipole interaction. The C_8 term describes both a dispersion and induction term. The induction term is frequently described as the permanent quadrupole-induced dipole moment interaction. It should be noted, however, that atoms are spherically symmetric and do not have permanent moments. Only when the degeneracy is lifted by some perturbation, such as the interaction with another atom, does it become meaningful to talk about the permanent moments of the atomic wave function, because the wave function then corresponds to one symmetry component of a degenerate state. In general, the C_n values are determined by the occupation of the two fragments [4]. (By occupation we mean the distribution of electrons in the orbitals without regard to spin coupling.) The $^4\Sigma^+$ and $^6\Sigma^+$ states of NO have similar C_n values, since they involve different spin couplings from the same occupation. The $^6\Pi$ state, which is derived from a different occupation, has somewhat different C_n values. We consider in this work whether computational approaches that use an individual atomic component even at infinite separation amplify this difference in C_n values. That is, is it necessary to use a computational approach that evolves into spherical atoms without any permanent moments at large r values?

2. Methods

We use the nitrogen basis set of [5] (denoted GTO-2) with the g function deleted. The basis set is derived from the ($11s\ 7p$) primitive set of Salez and Veillard [6] that is contracted to [$7s\ 5p$]. To improve the description of the polarizabilities, the valence basis set is supplemented with a diffuse s, p and two diffuse d functions. In order to account for correlation, the basis is supplemented with two d and two f functions, giving a final basis of the form ($12s\ 8p\ 4d\ 2f$)/[$8s\ 6p\ 4d\ 2f$]. As was shown in [5], this basis set accurately describes the polarizability of nitrogen atom; our best computed value of 7.21 a_0^3 is 97% of the value recommended by Miller and Bederson [7]. In addition, the basis set is sufficiently complete that it has less than one cm^{-1} of BSSE at the van der Waals minimum of the $^7\Sigma_u^+$ state of N_2.

Basis set studies show that an even larger oxygen basis set is required to obtain equivalent accuracy. We use the ($13s\ 8p$) set of Partridge [8], which is contracted to [$7s\ 5p$] and supplemented with two diffuse s, two diffuse p and a ($4d\ 2f$) polarization set. The exponents are: $\alpha(s) = 0.08$ and 0.032, $\alpha(p) = 0.051$ and 0.02, $\alpha(d) = 2.22$, 0.874, 0.345, and 0.143, and $\alpha(f) = 2.22$ and 0.784. After contraction the basis set is of the form ($15s\ 10p\ 4d\ 2f$)/[$9s\ 7p\ 4d\ 2f$]. At the coupled-pair functional [9] (CPF) level the polarizability is 5.14 a_0^3, or 95% of the recommended value [7]. Note that the polarizability is computed by reducing the symmetry of the atom to $C_{\infty v}$, and taking the weighted average of the polarizability of the $^3\Sigma^-$ and $^3\Pi$ components of the asymmetric O atom. As we show in the next section, both the O and N atoms have very small BSSEs. Only the pure spherical harmonic components of the basis functions are used.

The $^4\Sigma^+$, $^6\Sigma^+$, and $^6\Pi$ states of NO are derived from ground state atoms, N ($2p^3\,{}^4S^\circ$) and O ($2p^4\,{}^3P$). The valence occupations are

$$^6\Sigma^+, {}^4\Sigma^+ \quad 5\sigma^2 6\sigma^1 1\pi^2 2\pi^2 \tag{1}$$

and

$$^6\Pi \quad 5\sigma^1 6\sigma^1 1\pi^3 2\pi^2, \tag{2}$$

where the 5σ and 1π orbitals are predominantly O $2p$-like and the 6σ and 2π orbitals are N $2p$-like. Thus the Σ and Π states differ only in the orientation of the doubly occupied O $2p$ orbital.

A principal concern in determining the long-range portion of the NO potentials is whether or not to constrain the O $2p$ orbitals to be equivalent. In the limit of a full configuration-interaction calculation, the energy of the $^6\Sigma^+$ and $^6\Pi$ states will be identical, regardless of whether the $2p\sigma$ and $2p\pi$ orbitals are constrained to be equivalent asymptotically. However, this is not the case in truncated CI expansions, and the difference can be particularly large at the SCF level. Thus, one measure of the accuracy of any correlation method is the degree to which these two states are treated equivalently. It is straightforward to constrain the O $2p$ orbitals to be equivalent at large r using the state-averaged complete-active-space SCF (SA-CASSCF) approach by optimizing the orbitals for

$$E = 1/3E(^6\Sigma^+) + 2/3E(^6\Pi).$$

While this has the advantage of correctly dissociating to a symmetric O atom, it does not describe the orbital relaxation at short r quite as well as the SCF calculations for the individual states. However, just as correlation improves the description based on SCF-derived orbitals at long range, correlation improves the description based on SA-CASSCF-derived orbitals at short r. Even though the SA-CASSCF approach ensures equivalence of the orbitals, single-reference based correlation approaches using these orbitals may still result in different asymptotic energies for the $^6\Sigma^+$ and $^6\Pi$ states. Equivalence at the correlated level can be achieved by including all single and double excitations away from the three orientations of the O doubly occupied orbital, i.e. the SCF occupations for the $^6\Sigma^+$, $^6\Pi_x$ and $^6\Pi_y$ states (including only those configurations of the appropriate symmetry in the expansion). Since two of the three references are of the wrong symmetry and differ from the reference of the correct symmetry by a single excitation, inclusion of the other two references represents adding certain classes of triple excitations relative to the reference of the correct symmetry.

To address the question of the importance of constraining the O $2p$ orbitals at long range, we have employed two approaches in our study of the sextet states of NO. In the first, separate SCF calculations are performed for each state and then more extensive correlation is included using either the SDCI or CPF method. Since our earlier study of the $^7\Sigma_u^+$ state of N_2 indicated that correlation of the N $2s$ electrons significantly affected the potential, we correlated both the N $2s$ and O $2s$ electrons, resulting in an eleven-electron treatment. For the single reference-based calculations, we used the first-order interacting space restriction [10] to reduce the size of the CI expansions. For the $^6\Pi$ state, this restriction reduces the SDCI expansion from 298 206 to 75 336 CSFs without significantly affecting the spectroscopic constants. Our second approach involves a multireference CI(MRCI) from the three references described above using the

SA-CASSCF orbitals. This treatment ensures the equivalence of the energies of the $^6\Sigma^+$ and $^6\Pi$ states at large r values, but results in a much larger CI expansion of 611 260 CSFs for the $^6\Pi$ state. (Note that it is no longer possible to use the first-order interacting space restriction and still ensure equivalence of the two solutions.) Considering that the MRCI treatment results in expansions almost an order of magnitude larger than those in the single-reference approach using the first-order interacting space, it is important to assess whether these constraints significantly affect the potentials.

Since the $^4\Sigma^+$ state is not well described by a single configuration, we consider this state using only a CASSCF/MRCI approach. Calculations on the sextet states demonstrate that for high levels of correlation treatment it is not necessary to constrain the $2p\sigma$ and $2p\pi$ orbitals of oxygen to be equivalent. Therefore, the CASSCF orbitals for the $^4\Sigma^+$ state were optimized without any constraints. In the CASSCF calculations it was necessary to keep the $2p\sigma$ orbital in the inactive space: the orbital occupation is so close to 2.0 that otherwise the $2s$ and $2p\sigma$ orbitals mix making it difficult to consistently define the reference space as r varies. Thus the CASSCF calculation for the $^4\Sigma^+$ state has the five remaining $2p$ electrons distributed in five $2p$ orbitals. The MRCI calculations use all of the configurations in the CASSCF as references. As for the sextet states, eleven electrons are correlated in the MRCI calculations. We estimate the importance of higher excitations using the multireference analog of the Davidson correction (+Q) [11].

The BSSE is computed using the counterpoise method [12] with the full ghost orbital basis included. For the O atom the BSSE for the $2p\sigma^2 2p\pi^2$ and $2p\sigma^1 2p\pi^3$ occupations are significantly different. Thus at each r value we compute the BSSE at the SDCI, SDCI + Q and CPF levels for N atom and for both O atom configurations. The SDCI + Q BSSE values are less precise, which introduces some noise into these already small values. Since the CPF and SDCI + Q potentials are nearly congruent, we use the CPF BSSEs to correct the MRCI + Q potentials. The total BSSE is computed using the appropriate level of correlation treatment and orientation of the doubly occupied O $2p$ orbital.

The spectroscopic constants were calculated from a quadratic fit in $1/r$. The calculations were performed using the MOLECULE-SWEDEN program system [13] on the NAS Facility CRAY Y-MP/832.

3. Results and discussion

In Table 1 we compare the $^6\Sigma^+$ and $^6\Pi$ potentials as a function of level of treatment. The SCF results (not shown) have no van der Waals well and are about 2 000 cm^{-1} more repulsive at short r; hence correlation both softens the repulsive inner wall and is necessary to describe the dispersion at long range. The SDCI + Q and CPF results are in good agreement, differing by less than 1 cm^{-1} in the region of the molecular well, and by less than 100 cm^{-1} at the shortest bond lengths considered. A comparison of the SDCI and SDCI + Q (or CPF) results shows that higher excitations make an important contribution to the description of the potential. A comparison of the SDCI and MRCI results shows that the effect of averaging for two states in the orbital optimization and expanding the CI reference list to produce a spherically symmetric O atom at large r has only a very small effect on the results. In fact, averaging makes essentially no difference for the $^6\Sigma^+$ state and only a very small difference for the

Table 1. Comparison of the NO $^6\Sigma^+$ and $^6\Pi$ potentials at different levels of treatment, in cm^{-1}

r (a_0)	SDCI	SDCI + Q	CPF	MRCI	MRCI + Q
$^6\Sigma^+$					
3.50	13030.37	12666.69	12597.79	13086.64	12441.26
4.00	5101.29	4897.51	4849.03	5093.86	4778.13
4.50	1904.53	1802.54	1778.53	1894.75	1747.77
5.00	657.69	605.16	594.57	652.27	580.94
5.50	194.24	164.96	160.28	191.63	153.89
6.00	34.18	16.56	14.29	32.94	11.10
6.25	2.33	−11.66	−13.31	1.47	−15.64
6.50	−13.99	−25.23	−26.47	−14.59	−28.20
6.75	−21.33	−30.44	−31.40	−21.73	−32.70
7.00	−23.61	−31.03	−31.79	−23.88	−32.80
7.25	−23.16	−29.24	−29.86	−23.34	−30.64
7.50	−21.38	−26.37	−26.88	−21.49	−27.48
8.00	−16.64	−20.02	−20.38	−16.68	−20.72
9.00	−8.86	−10.47	−10.65	−8.86	−10.73
10.00	−4.67	−5.47	−5.57	−4.67	−5.58
11.00	−2.63	−3.06	−3.12	−2.63	−3.10
12.00	−1.56	−1.81	−1.85	−1.56	−1.81
15.00	−0.44	−0.50	−0.51	−0.44	−0.48
99.00	0.00	0.00	0.00	0.00	0.00
$^6\Pi$					
3.50	13553.08	13272.02	13196.21	13519.98	13101.46
4.00	5195.90	5073.78	5046.02	5179.57	5015.38
4.50	1901.63	1841.20	1829.26	1892.54	1817.14
5.00	648.81	615.15	609.58	643.39	603.51
5.50	193.20	172.75	169.98	189.88	166.48
6.00	38.19	25.09	23.56	36.15	21.50
6.25	7.43	−3.18	−4.36	5.83	−5.93
6.50	−8.48	−17.12	−18.05	−9.73	−19.24
6.75	−15.86	−22.92	−23.67	−16.84	−24.56
7.00	−18.47	−24.26	−24.87	−19.24	−25.54
7.25	−18.52	−23.28	−23.79	−19.13	−24.28
7.50	−17.30	−21.22	−21.64	−17.78	−22.00
8.00	−13.64	−16.32	−16.62	−13.94	−16.80
9.00	−7.46	−8.75	−8.91	−7.59	−8.93
10.00	−4.06	−4.73	−4.81	−4.12	−4.78
11.00	−2.34	−2.72	−2.77	−2.38	−2.73
12.00	−1.43	−1.65	−1.68	−1.45	−1.63
15.00	−0.40	−0.45	−0.47	−0.40	−0.42
99.00	0.00	0.00	0.00	0.00	0.00

$^6\Pi$ state for r values greater than 7.5 a_0, where the symmetric and asymmetric solutions might be expected to differ most.

While the MRCI results agree well with the SDCI values, the MRCI + Q and SDCI + Q (or CPF) results differ slightly, especially at smaller r values. This is probably due to the use of less optimal orbitals in the MRCI calculations, which reduces the weight of the reference in the final wave function. In order to obtain spherical atoms at long range, we have imposed a constraint in the MRCI calculation that artificially decreases the weight of the reference, but this is compensated for by a larger correlation energy due to the inclusion of additional configurations. This effect becomes large as r decreases, since the orbital relaxation becomes more important. This results in a +Q correction that tends to increasingly overestimate the effect of higher excitations as r decreases. Our calculations thus suggest that it may actually be preferable to use inequivalent orbitals, especially considering that the single reference-based SDCI + Q and CPF give quantitative results at a fraction of the cost of doing the much larger CASSCF/MRCI calculations. The success of the SDCI + Q or CPF levels, based on the inequivalent $2p$ orbitals, is perhaps a consequence of the fact that while the $^6\Sigma^+$ and $^6\Pi$ asymptotes differ by 452 cm^{-1} at the SCF level, they differ by only 2 and 19 cm^{-1} at the SDCI + Q and CPF levels, respectively.

We feel that the CPF potentials are the most reliable, since the CPF method includes the effect of higher excitations more rigorously than the +Q correction. However, as noted above, the difference between the SDCI + Q and CPF potentials is very small, which suggests that we have accounted for most of the effects of higher excitations. Thus the largest source of errors in the calculation is expected to arise from limitations of the one-particle basis sets. Basis set incompleteness will make the potentials too shallow and BSSE will make them deeper. Since we account for BSSE, our D_e values are probably lower bounds and are within a few cm^{-1} of the true well depths. In Table 2 we tabulate the CPF potentials for the $^6\Sigma^+$ and $^6\Pi$ states corrected for BSSE. The BSSE at the CPF level for N atom is less than 1 cm^{-1} in the region of r_e, and increases to only 23 cm^{-1} at 3.5 a_0. The O BSSE is somewhat larger, being 2 (3) cm^{-1} for the $2p\sigma^1 2p\pi^3$ ($2p\sigma^2 2p\pi^2$) occupation at 7.0 a_0, increasing to 33 (57) cm^{-1} at 3.5 a_0.

Table 2. NO $^6\Sigma^+$ and $^6\Pi$ state CPF potentials, in cm^{-1}, after correction for BSSE

r (a_0)	$^6\Sigma^+$	$^6\Pi$
3.50	12676.70	13250.37
4.00	4895.56	5076.21
4.50	1808.11	1847.64
5.00	613.94	621.34
5.50	172.99	177.74
6.00	22.59	28.76
6.25	−6.49	−0.03
6.50	−20.76	−14.37
6.75	−26.54	−20.48
7.00	−27.62	−22.08
7.25	−26.27	−21.33
7.50	−23.80	−19.49
8.00	−18.11	−14.98
9.00	−9.43	−7.93
10.00	−4.89	−4.19
11.00	−2.66	−2.32
12.00	−1.52	−1.35
15.00	−0.37	−0.33
99.00	0.00	0.00

While the O atom BSSE is larger than for N atom, the total error is sufficiently small that the counterpoise-corrected potentials should be accurate.

Since the repulsive term is accurately accounted for even at the SCF level, the error in the interaction strength is approximately proportional to the error in the product of the dipole polarizabilities of N and O. Thus our well depth should have an error of about 3 cm^{-1} (or 8%), as we obtain about 97% of $\alpha(N)$ and 95% of $\alpha(\mathrm{O})$. This is probably an upper bound to our error, since basis set tests indicate that D_e increases more slowly than the product of the polarizabilities, which is consistent with empirical models where the attractive term is damped for r values near r_e. In Table 3 we tabulate the MRCI and MRCI + Q $^4\Sigma^+$ potentials, with and without correction for BSSE. As for the sextet states, the +Q correction has a significant effect on the potential. The MRCI + Q results are expected to be more accurate based on the fact that the SDCI + Q and CPF potentials are in excellent agreement for the $^6\Sigma^+$ and $^6\Pi$ states. Higher levels of theory are not expected to produce potentials that deviate significantly from the MRCI + Q results. At long range ($r > 9.0\,a_0$) the $^4\Sigma^+$ and $^6\Sigma^+$ potentials are very similar, since the wave functions are dominated by the same occupation—compare the SDCI + Q potential in Table 1 with the MRCI + Q potential in Table 3. The $^6\Pi$ state, which has a different occupation, is noticeably different in the large r region.

Ideally, C_6 and C_8 could be determined by fitting the long range part of the potentials. Unfortunately, the energy differences are sufficiently small that the "noise" in the computed potentials makes the parameters very sensitive to the fitting procedure. Overall, we find that the average C_6 value ranges from about

Table 3. The NO $^4\Sigma^+$ potential, in cm^{-1}

r (a_0)	Without BSSE correction		With BSSE correction	
	MRCI	MRCI + Q	MRCI	MRCI + Q
3.50	11264.83	9899.70	11340.26	9978.61
4.00	5098.99	4700.74	5143.13	4747.27
4.50	2088.08	1952.58	2116.00	1982.17
5.00	787.72	730.55	805.96	749.92
5.50	265.29	236.10	277.29	248.82
6.00	69.09	51.86	76.95	60.17
6.25	26.18	12.45	32.65	19.27
6.50	2.07	−9.05	7.50	−3.34
6.75	−10.65	−19.76	−6.02	−14.90
7.00	−16.59	−24.11	−12.62	−19.94
7.25	−18.62	−24.84	−15.20	−21.26
7.50	−18.48	−23.65	−15.54	−20.57
8.00	−15.53	−19.10	−13.36	−16.83
9.00	−8.80	−10.55	−7.62	−9.33
10.00	−4.75	−5.65	−4.10	−4.97
11.00	−2.71	−3.21	−2.27	−2.75
12.00	−1.63	−1.93	−1.33	−1.60
15.00	−0.48	−0.56	−0.35	−0.42
99.00	0.00	0.00	0.00	0.00

Table 4. Summary of spectroscopic constants for the $^6\Sigma^+$, $^4\Sigma^+$ and $^6\Pi$ states of NO. The values in parentheses include the BSSE correction

	SDCI	SDCI + Q	CPF
$^6\Sigma^+$			
$r_e\,(a_0)$	7.078 (7.139)	6.930 (6.997)	6.911 (6.977)
$D_e\,(\mathrm{cm}^{-1})$	23.7 (19.9)	31.1 (26.8)	31.9 (27.6)
$^6\Pi$			
$r_e\,(a_0)$	7.132 (7.183)	7.011 (7.051)	6.998 (7.037)
$D_e\,(\mathrm{cm}^{-1})$	18.7 (16.2)	24.3 (21.5)	24.9 (22.1)
$^4\Sigma^+$			
	MRCI	MRCI + Q	
$r_e\,(a_0)$	7.355 (7.451)	7.212 (7.281)	
$D_e\,(\mathrm{cm}^{-1})$	18.8 (15.6)	24.9 (21.3)	

89 to 92% of the value determined by Zeiss and Meath [14]. This is consistent with the fact that our computed product $\alpha(\mathrm{N}) \times \alpha(\mathrm{O})$ is 92% of the best value. In addition, we find the C_8 value for the $^6\Sigma^+$ state is much larger than for the $^6\Pi$ state; this much larger difference in C_8 than C_6 reflects the effect of the "permanent quadrupole" arising from the different orientations of the asymmetric O atom.

In Table 4 we summarize the computed r_e and D_e values for the three van der Waals states of NO. The binding energies differ only slightly. The $^6\Sigma^+$ state is more stable than the $^6\Pi$ state, probably due to the improved shielding of the nuclei resulting from having one additional σ electron. The $^4\Sigma^+$ state might have been expected to be the more strongly bound, as the lower spin could lead to some additional covalent bonding configurations; in this regard we note that the $^4\Pi$ state is a chemically bound state. We suggest that the $^4\Sigma^+$ state is less strongly bound than the $^6\Sigma^+$ state, because it mixes in some unfavorable low-spin atomic coupling with the covalent bonding configurations.

4. Conclusions

We have studied the $^6\Sigma^+$, $^6\Pi$ and $^4\Sigma^+$ van der Waals states of NO. Correlation must be included and basis set superposition errors must be accounted for to obtain an accurate potential. However, we find that it is unnecessary to force spherical symmetry on the oxygen atom at large r values; this procedure simply leads to much larger CI expansions and makes the +Q correction less reliable. The $^4\Sigma^+$ and $^6\Sigma^+$ states have very similar potentials at large r, as expected, since they arise from the same occupation. At short r the $^6\Sigma^+$ state is the most stable, with the $^4\Sigma^+$ and $^6\Pi$ states having similar but slightly smaller binding energies. The potentials are accurate even at the shortest r values (3.5 a_0) and allow the computation of collision integrals for the high-spin states dissociating to $\mathrm{N}(^4S^\circ) + \mathrm{O}(^3P)$ that are important for the computation of the transport properties of high-temperature air.

References

1. Levin E, Partridge H, Stallcop JR: J Thermophys Heat Trans, in press
2. Buckingham AD, Fowler PW, Hutson JM (1988) Chem Rev 88:963
3. Bussery B, Aubert-Frécon M (1985) J Chem Phys 82:3224
4. Chang TY (1967) Rev Mod Phys 39:911
5. Partridge H, Langhoff SR, Bauschlicher CW (1986) J Chem Phys 84:6901
6. Salez C, Veillard A (1968) Theor Chim Acta 11:441
7. Miller TM, Bederson B (1978) Adv Atom Mol Phys 13:1
8. Partridge H (1989) J Chem Phys 90:1043
9. Ahlrichs R, Scharf P, Ehrhardt C (1985) J Chem Phys 82:890
10. Bunge A (1970) J Chem Phys 53:20; McLean AD, Liu B (1973) ibid 58:1066; Bender CF, Schaefer HF (1971) ibid 55:7498
11. Langhoff SR, Davidson ER (1974) Int J Quantum Chem 8:61; Blomberg MRA, Siegbahn PEM (1983) J Chem Phys 78:5682
12. Boys SF, Bernardi F (1970) Mol Phys 19:553
13. MOLECULE-SWEDEN is an electronic structure program system written by Almlöf J, Bauschlicher CW, Blomberg MRA, Chong DP, Heiberg A, Langhoff SR, Malmqvist P-Å, Rendell AP, Roos BO, Sigebahn PEM, Taylor PR
14. Zeiss GD, Meath WJ (1977) Mol Phys 33:1155