

SCF-CI Calculations of the Potential Energy Curve and One-Electron Property Curves of the $X^1\Sigma_g^+$ Ground State of N_2

William I. Ferguson

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

The energy and important one-electron properties of the nitrogen molecule are evaluated in the $^1\Sigma_g^+$ ground state for various internuclear separations near the equilibrium geometry, at the SCF-CI level. Both our Roos CI and Graphical Unitary Group (GUG) programs were used in performing single and multiple root CI computations. The one-electron properties included are the quadrupole and hexadecapole moments (both with respect to the centre of mass) and the electric field gradient at the N nucleus. Dependence of the properties upon the vibrational quantum number are evaluated using the Dunham analysis scheme.

Key words: SCF-CI – Nitrogen (N_2) – Graphical unitary group (GUG).

1. Introduction

The purpose of these calculations was to obtain highly accurate one-electron properties of the N_2 molecule from large scale SCF-CI calculations and to test the effectiveness of the multi-root algorithm we have devised recently [1] within Graphical Unitary Group Approach (GUGA) [2]. The SCF and CI values obtained are compared with those derived from experimental results, where available. The properties considered in this work are the quadrupole and hexadecapole moments and the electric field gradient.

The multipole moments of molecules are of general importance in the wide fields of intermolecular forces and light scattering. They are particularly important in determining the form of the collision-induced far infra-red spectrum of homonuclear diatomics such as N_2 [3, 4, 5]. Indeed, the principle experimental

results use this method (or microwave line-broadening effects) to derive the quadrupole and hexadecapole moments.

The electric field gradients at the nuclei are of relevance in NMR and NQR experiments [6], in which they determine the line shapes, and in the magnetic hyperfine splitting of the microwave spectrum of $^{14}\text{N}^{14}\text{N}$ [7].

The derivatives of these properties may also be calculated and, using the property surface in conjunction with the energy surface, can be used to obtain vibrationally averaged values of properties, in addition to the vibrational quantum number dependence of these properties. The derivatives of the multipole moments are again important in the discussion of intermolecular forces and light scattering phenomena, but are unfortunately difficult to access.

The nitrogen molecule has been fairly extensively studied at the equilibrium geometry including several calculations of SCF one-electron properties at the Hartree–Fock limit [8–13]. Calculations of the properties as a function of distance at the SCF level have been performed by Nesbet [11]. Correlated wavefunction calculations of the properties have been performed by Billingsley and Krauss [12], Dunning et al. [9] and more recently by Amos [13].

The calculations of Dunning et al. [9] (using the generalised valence-bond method) and Amos [13] (using our [14] “direct” CI program) investigated the molecular properties as a function of separation. The direct comparison of *ab initio* and experimental data including vibrational corrections to observables of the correlated wavefunctions is shown by both to be necessary.

2. Calculations

The basis adopted consisted of the standard Dunning [15] contraction yielding a $\text{N}(5s3p2d)$ set with d function scaling factors of 0.8. This produces an SCF energy at the equilibrium geometry of -108.9768 Hartrees at $R_e = 2.0197$ Bohr, compared with the near Hartree–Fock limit value [8] of -108.9956 Hartrees at $R_e = 2.0132$ Bohr. The R_e value obtained by experiment is 2.0744 Bohr [16]. The SCF energy and property values are included in Table 1. The values so

Table 1. Potential energy surface and property surfaces (SCF) for the $\text{N}_2 X^1\Sigma_g^+$ ground state configuration (in a.u.)

R/Bohr	E (SCF)/Hartree	$q_N(z^2)$ /a.u.	$\theta(z^2)$ /a.u.	$\Phi(z^4)$ /a.u.
1.9	-108.960386475	1.4118	-1.2115	-6.7656
1.95	-108.971365470	1.3915	-1.1421	-6.9607
2.0	-108.976115510	1.3659	-1.0711	-7.1410
2.05	-108.975636045	1.3360	-0.9987	-7.3040
2.1	-108.970781752	1.3026	-0.9247	-7.4477
2.15	-108.962282929	1.2663	-0.8493	-7.5703
2.2	-108.950765508	1.2278	-0.7725	-7.6701

Table 2. Potential energy surface and property surfaces (CI 1) for the $N_2^+ \Sigma_g^+$ ground state configuration (in a.u.)

R/Bohr	E (CI)/Hartree	$q_N(z^2)/a.u.$	$\theta(z^2)/a.u.$	$\Phi(z^4)/a.u.$
1.9	-109.304306030	1.2790	-1.3360	-6.5122
1.95	-109.319007449	1.2552	-1.2787	-6.7009
2.0	-109.32751510	1.2262	-1.2203	-6.8765
2.05	-109.331049109	1.1932	-1.1608	-7.0369
2.1	-109.330226183	1.1569	-1.1000	-7.1804
2.15	-109.325844250	1.1180	-1.0380	-7.3055
2.2	-109.318520522	1.0772	-0.9750	-7.4106

obtained are in good agreement with the best SCF values to date and the expected Hartree–Fock limit values.

The CI wavefunctions evaluated here were obtained using our “direct” CI program [14] and our Graphical Unitary Group Approach program [2]. In the first set of single root function CI calculations (CI 1), using the Roos approach, the SCF wavefunction,

$$\Phi_0 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^{x^2} 1\pi_u^{y^2}|,$$

in addition to all singles and doubles excitations formed the CI expansion (with no frozen orbitals). This generated a total of 7604 spin-symmetry adapted configurations. The CI energy and one-electron property values are presented in Table 2. The CI wavefunction produced an equilibrium geometry of $R_e = 2.0639$ Bohr with a corresponding total energy of -109.331 Hartrees, in good agreement with experiment, and corresponding to a bond lengthening beyond the SCF level, as expected. In the second series of CI calculations using the GUG method [2] we adopted 5 root functions, including all singles plus doubles excitations out of these (in the full spin-space) to form the CI expansion (CI 2). A multi-root algorithm developed by us recently was used to construct the necessary “distinct row table” for use in the calculation. Orbitals 1 and 2 and orbitals 47 to 52 were frozen in the computations to restrict the CI expansion length to a tractable size for our machine. The 5 roots included in the second CI calculation were:

$$\Phi_0^1 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^{x^2} 1\pi_u^{y^2}|,$$

$$\Phi_0^2 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^{x^2} 1\pi_g^{y^2}|,$$

$$\Phi_0^3 = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_g^{x^2} 1\pi_u^{y^2}|,$$

$$\Phi_0^{4,5} = |1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^x 1\pi_u^y 1\pi_g^x 1\pi_g^y|,$$

i.e. those forming the most important doubles configurations in the singles plus doubles single root calculations of CI 1. This generated a total of 17505 spin-symmetry adapted configuration state functions in CI 2. An energy minimum of -109.2995 Hartrees at $R_e = 2.0900$ Bohr was thus obtained. The higher energy obtained in this case, compared to CI 1 of course reflects the fact that only

Table 3. Potential energy surface and property surfaces (CI 2) for the $N_2 \ ^1\Sigma_g^+$ ground state configuration (in a.u.)

R/Bohr	E (CI)/Hartree	$q_N(z^2)$ /a.u.	$\theta(z^2)$ /a.u.	$\Phi(z^4)$ /a.u.
1.9	-109.26592127	1.2198	-1.3621	-6.3895
1.95	-109.28242451	1.1928	-1.3094	-6.5676
2.0	-109.29285979	1.1601	-1.2563	-6.7331
2.05	-109.29822520	1.1228	-1.2027	-6.8839
2.1	-109.29937398	1.0819	-1.1486	-7.0186
2.15	-109.29703446	1.0380	-1.0941	-7.1356
2.2	-109.29183096	0.9918	-1.0390	-7.2335

44 SCF orbitals were kept active at the CI stage. CI values for the energy and one-electron properties over the range of R are presented in Table 3.

A Dunham [17] analysis of the resulting energy and property surfaces was subsequently carried out to obtain the vibrationally averaged values of the one-electron properties and their vibrational dependence.

The summary of this analysis is included in Table 4 for SCF and CI results, in addition to the experimental values.

The spectroscopic constants obtained show a marked improvement at the CI level. As expected, the multiple root spectroscopic values appear slightly better than those obtained using a single root. However, again the first anharmonic constants for both CI sets are far from spectroscopic in quality. For this reason, experimental spectroscopic values were used in conjunction with the one-electron

Table 4. Values for spectroscopic constants and other properties for the $N_2 \ X^1\Sigma_g^+$ state from the CI calculation

Property	Experimental	This calc. (SCF)	This calc. (CI 1)	This calc. (CI 2)
R_e /Bohr	2.0744 [16]	2.01960	2.06388	2.09094
B_e /cm ⁻¹	1.9982 [16]	2.109	2.020	1.968
ω_e /cm ⁻¹	2358 [16]	2950	2418	2305
$\omega_e X_e$ /cm ⁻¹	14.19 [16]	445.661	-142.602	7.190
α_e /cm ⁻¹	0.0173 [16]	0.052	0.021	-0.009
$\theta(z^2)$ /a.u.	-1.0253 [20]	-0.9637	-1.1307	-1.1764
		+0.023 ($\nu + \frac{1}{2}$)	+0.019 ($\nu + \frac{1}{2}$)	+0.016 ($\nu + \frac{1}{2}$)
$\Phi(z^4)$ /a.u.	4.8 to 11.2 [4]	-7.3755	-7.1100	-6.9514
		-0.014 ($\nu + \frac{1}{2}$)	-0.017 ($\nu + \frac{1}{2}$)	-0.015 ($\nu + \frac{1}{2}$)
$q_N(z^2)$ /a.u.	1.141 [13, 18]	+1.3205	1.1755	1.1033
		-0.014 ($\nu + \frac{1}{2}$)	-0.014 ($\nu + \frac{1}{2}$)	-0.016 ($\nu + \frac{1}{2}$)

Conversion factors:

Quadrupole moment 1 a.u. = 4.486613×10^{-40} Cm²

Hexadecapole moment 1 a.u. = 1.256378×10^{-60} Cm⁴

Electric field gradient 1 a.u. = 9.7171×10^{21} Vm⁻²

property curves to derive the vibrational dependence of the important properties. The slightly large value for R_e obtained using CI 2 is doubtless due to the adoption of a frozen $1s$ core set on both N atoms. The differences between SCF and CI values are most obvious in the case of Θ and q_N , as has been noted previously in the calculations of Billingsley and Krauss [12], Dunning et al. [9] and Amos [13]. The first derivatives of the one-electron properties again show a marked improvement with the use of a correlated wavefunction particularly in the value of $\partial\theta/\partial\xi$ (where $\xi = (r - r_e)/r_e$).

Electric field gradient values may in theory be obtained experimentally from the nuclear quadrupole coupling term eQq/h , which can be measured from the line shapes in NQR studies of solid N_2 [6] and also in ^{14}N NMR microwave spectra [6], where it is evident from the line broadening due to relaxation effects. Unfortunately, no reliable value for the nuclear quadrupole, Q_N , of ^{14}N is available and estimated values have been based upon previous *ab initio* calculations, correlated with NMR experimental values of eQq/h . The estimated values are variable [6]. An NQR study of solid N_2 indicates a value in $^{14}N^{14}N$ of 5.39 ± 0.05 MHz [18]. The calculated values of q would thus provide values for Q_N of $0.01953 \times 10^{-28} \text{ m}^2$ and $0.02084 \times 10^{-28} \text{ m}^2$ respectively for the CI 1 and CI 2 computations, in good agreement with the previous accurate correlated wavefunction calculations.

The quadrupole moment may, in principle, be obtained in one of several ways. The most direct method, applicable only to non-dipolar molecules, is the method of electric field gradient induced birefringence [19, 20]. The value of the quadrupole moment so obtained is $-4.6 \times 10^{-40} \text{ Cm}^2$, compared with our values of $5.03 \times 10^{-40} \text{ Cm}^2$ and $5.24 \times 10^{-40} \text{ Cm}^2$ for CI 1 and CI 2 respectively. The discrepancy in these CI results with experiment is thought to be due to the neglect of hyperpolarizability terms in the experimental setup [13]. The quadrupole moment may also be obtained from the rotational g factor and the magnetic anisotropy [21]. However, such values are likely to prove highly unreliable.

Finally, all the molecular multipole moments may, again in principle, be obtained from far infra-red collision-induced absorption [3, 4, 5]. This approach again, however, yields values which are unreliable, depending as they do on the form of intermolecular potential and scattering diameter chosen in the model [4]. The method produces quadrupole moments in the range 3 to $5 \times 10^{-40} \text{ Cm}^2$ and hexadecapole moments in the range 6 to $14 \times 10^{-60} \text{ Cm}^4$ [4]. The SCF and CI values fall within this range and it might be expected that the CI values of $8.94 \times 10^{-60} \text{ Cm}^4$ (CI 1) and $8.74 \times 10^{-60} \text{ Cm}^4$ (CI 2) for the hexadecapole moment are reasonably accurate.

3. Conclusion

Large scale SCF-CI calculations on the N_2 ground electronic state have shown excellent agreement with experimental results for several of the interesting and important one-electron properties. Indeed, it may be expected that, due to the

many difficulties involved in the experimental techniques and the analysis of resulting data, that our CI values for vibrationally averaged one-electron properties are, in fact, more accurate than the corresponding experimentally obtained ones. This is born out by the surprisingly high degree of agreement between the single and multiple root calculations. The correlation between the vibrational quantum number dependence for CI 1 and CI 2 indicate that the wavefunctions (especially that of CI 2) are very accurate indeed.

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