Full relativistic calculations of the quadrupole and electric field gradients for C_2, N_2, and O_2*

Zhang Li(张 莉) and Zhu Zheng-He(朱正和)†

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, *China*

(Received 10 July 2012; revised manuscript received 29 August 2012)

In the present work we calculate the energies, quadrupole moments, and electric field gradients (EFGs) of molecules C_2, N_2, and O_2 based on the DIRRCI method with basis aug-cc-pVTZ-DK. We prove that the quadratic force constant k_2 is the product of charge and EFG at its equilibrium nuclear distance. The dipole charge distributions for these symmetrical molecules are all in equilibrium, however, the quadrupole charge distributions are far from equilibrium; among these, there is the most remarkable deviation from equilibrium for N_2, for its many charges concentrate on two sides of the molecule, which is in agreement with the well-known characteristic of the nitrogen molecule. The relativistic effect is remarkable even for the same period.

Keywords: quadrupole moment, electric field gradients, the full relativistic quantum mechanics

PACS: 31.15.–p, 31.15.ap, 02.20.–a **DOI:** 10.1088/1674-1056/22/2/023102

1. Introduction

In recent years much effort has been devoted to the development of efficient and accurate relativistic schemes for the investigation of molecular properties, particularly, the electric field gradient (EFG) has received special attention.[1,2] Since the EFG operator depends on the electron–nucleus distance r as r^{-3}, this property is affected by relativistic effects much earlier than dipole moments or polarizabilities.[1] Nowadays such calculations are possible even with a four-component coupled cluster method.[3] Concerning relativistic corrections to electrical properties such as dipole moment, quadrupole moment, and EFG, a lot of calculations have been reported in the literature.[4–8] Electric polarizability is also associated with important characteristics of electronic structure. The EFGs and potential energy functions (PEFs) have been used to estimate the ^{14}N nuclear quadrupole coupling contants (NQCCs) in the two electronic states of the nitrogen molecule.[9] However, as mentioned by authors, up to now there have been no data to be immediately compared with their ^{14}NQCCs in the states of N_2^+, as there has existed only a reliable knowledge of the electronic ground state of N_2. The shifts of the bond-stretching frequencies and the integrated vibrational fundamental band intensities for N_2, O_2, and D_2 adsorbed on the dehydrated LiX, NaLiX, and NaX zeolites were studied by FT-IR spectra and the effective electric fields in zeolite cavities were also reported,[10] which shows that the electric field is important for the formation of chemical bonds. However, that work has no calculation of electric field gradient (EFG). The present work proves that the quadratic force constant k_2 is the product of charge and EFG at its equilibrium nuclear distance.

There are two methods that can be used to expand the multipole moment,[11] i.e. in terms of a plane wave or irreducible tensor operators (ITOs). The general components of the multipole expansion are given by

$$Q_q^k = e\left[\frac{4\pi}{(2k+1)}\right]^{1/2} r^k \mathrm{Y}_q^k(\theta,\phi) = e r^k C_q^k(\theta,\phi), \qquad (1)$$

where $C_q^k(\theta,\phi)$ is Racah's normalized spherical harmonics which is defined as

$$C_q^k(\theta,\phi) = \left[\frac{4\pi}{(2k+1)}\right]^{1/2} \mathrm{Y}_q^k(\theta,\phi), \qquad (2)$$

Q_q^k is the k-rank tensor operator, if $k = 0, 1, 2, 3, \ldots$, it is called monopole, dipole, quadrupole, and octapole moments $\ldots$, respectively. For instance, if $k = 1$, we have $q = 1, 0, -1$, and correspondingly the $\mathrm{Y}_q^k(\theta,\phi)$ gives

$$\mathrm{Y}_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2}\frac{\chi+\mathrm{i}y}{r},\quad \mathrm{Y}_0^1 = \left(\frac{3}{4\pi}\right)^{1/2}\frac{z}{r},$$
$$\mathrm{Y}_{-1}^1 = \left(\frac{3}{8\pi}\right)^{1/2}\frac{\chi-\mathrm{i}y}{r}. \qquad (3)$$

As an example, from Eqs. (1), (2), and (3), the z component can be expressed as $Q_q^k = Q_0^1 = \mu_0^1 = ez$, in which the standard ITO is the same as the non-standard one. The components of the quadrupole can be expressed from spherical harmonics functions as $\mathrm{Y}_2^2(\theta,\phi)$, $\mathrm{Y}_1^2(\theta,\phi)$, $\mathrm{Y}_0^2(\theta,\phi)$, $\mathrm{Y}_{-1}^2(\theta,\phi)$, and $\mathrm{Y}_{-2}^2(\theta,\phi)$.

It is proved that only three principal components Q_{xx}, Q_{yy}, and Q_{zz} are nonzero.

This approach is motivated by the fact that the time reversal symmetry operation and the full relativistic quantum mechanical effects would be very pronounced in comparison with

*Project supported by the Fundamental Research Funds for the Central Universities.

†Corresponding author. E-mail: Zhuxm@scu.edu.cn

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some of the nonrelativistic methods. The main attention is focused on the computations of energies, quadrupole moments, and EFGs for C_2, N_2, and O_2 based on the full relativistic theory. In particular, there is an exploration of how to relate the force constants to EFGs.

2. Full relativistic theory

Symmetry plays an important role in quantum mechanical theory. There are three levels for the quantum mechanical method, i.e., nonrelativistic, relativistic, and the full relativistic quantum mechanics, and they are based on the single point group, the double group, and the full symmetry group or quaternion symmetry, respectively.[12–15]

In consideration of the equivalence of space and time, for the full relativistic theory based on the full symmetry group or quaternion symmetry, the time reversal symmetry operation is included in the symmetry group. As is well known, the product of two symmetry operators is represented by the product of the corresponding unitary matrices in the theory of group representation. However, the time reversal symmetry operation is an anti-unitary operator. The group including both space and time operations is called the full symmetry group, and their group representation is called a co-representation, in which the nomenclature is introduced by Wigner. The co-representation is not unitary representation; however, it is still possible to be broken down to an irreducible form. The third level, i.e., relativistic quantum mechanical theory based on the full symmetry group or quaternion symmetry was first used in the work by Saue and Jensen.[16,17]

A time reversal operator, also called a Kramer operator[12,14] is defined as

$$\hat{K}\psi(r,t) = \psi^*(r,-t). \tag{4}$$

If the Hamiltonian $\hat{H}$ is a real function of r, then

$$\begin{aligned}\hat{K}\hat{H}(r)\psi(r,t) &= \hat{H}^*(r)\psi^*(r,-t)\\ &= \hat{H}(r)\psi^*(r,-t)\\ &= \hat{H}\hat{K}\psi(r,t),\end{aligned} \tag{5}$$

i.e.,

$$[\hat{H},\hat{K}] = 0. \tag{6}$$

The commutator (3) is the necessary and sufficient condition for two operators $\hat{K}$ and $\hat{H}$ to have the same set of eigenfunctions, that is, the state is invariant to time reversal (motion reversal).

It is proved that the time reversal operator is anti-unitary,[12,15] i.e.,

$$\langle \hat{K}\psi/\hat{K}\phi\rangle = \langle\psi/\phi\rangle^* = \langle\phi/\psi\rangle. \tag{7}$$

It is also an anti-linear operator.

Kramer theorem[12,14] It can be proved that if $\hat{K}^2 = -1$ is corresponding to J value of a half odd integer, i.e. fermions, there will be the new double degeneracy by time reversal; and if $\hat{K}^2 = +1$ is corresponding to J value of an integer, i.e. bosons, then there will be no double degeneracy.

The time-independent Dirac equation is

$$\hat{h}_{\rm D}\psi = E\psi \ \text{ with } \ \hat{h}_{\rm D} = \beta' mc^2 + c(\boldsymbol{\alpha}\hat{\boldsymbol{p}}) + \hat{V}, \tag{8}$$

where

$$\boldsymbol{\alpha} = \begin{bmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{bmatrix} \ \text{ and } \ \beta' = \begin{bmatrix} 0 & 0 \\ 0 & 2\boldsymbol{I}_2 \end{bmatrix} \ \text{ with } \ \boldsymbol{I}_2 - 2\times 2. \tag{9}$$

Here, $\boldsymbol{I}_2$ is the unit matrix and Pauli spin matrices are as follows:

$$\boldsymbol{\sigma}_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}; \quad \boldsymbol{\sigma}_y = \begin{bmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{bmatrix}; \quad \boldsymbol{\sigma}_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{10}$$

If $\hat{V} = 0$, equation (8) will become the Dirac equation of free electrons.

Now, the time reversal operator is defined using another equivalent method, i.e., Kramer theorem[12,14] in which $\hat{K}^2 = -1$, that is, $\hat{K}^2\phi = -\phi = \bar{\phi}$, in which the state is recovered by operating time reversal twice, however, the wave function is changed to the negative; if $\hat{K}^2 = +1$, that is, $\hat{K}^2\phi = \phi$, in which the state is recovered by operating time reversal twice, the wave function is unchanged. Then ϕ and $\bar{\phi}$ are said to form a Kramer?s pair. Therefore, the operator can be expanded in terms of Kramer's partners $\{\phi\}$ and $\{\bar{\phi}\}$. For example, the Hermitian of a one-electron operator[16,17] is defined as

$$\begin{aligned}\hat{h}_{\rm D} &= \begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ -\boldsymbol{B}^* & \boldsymbol{A}^* \end{pmatrix}\\ &= \begin{pmatrix} \hat{V} & -\mathrm{i}c\hat{d}_z & 0 & -\mathrm{i}c\hat{d}_- \\ -\mathrm{i}c\hat{d}_z & -2mc^2+\hat{V} & -\mathrm{i}c\hat{d}_- & 0 \\ 0 & -\mathrm{i}c\hat{d}_+ & \hat{V} & \mathrm{i}c\hat{d}_z \\ -\mathrm{i}c\hat{d}_+ & 0 & \mathrm{i}c\hat{d}_z & -2mc^2+\hat{V} \end{pmatrix},\end{aligned} \tag{11}$$

where

$$\hat{d}_z = \frac{\partial}{\partial z}, \qquad \hat{d}_\pm = \frac{\partial}{\partial x} \pm \mathrm{i}\frac{\partial}{\partial y}. \tag{12}$$

It is easy to know

$$\boldsymbol{A} = \begin{pmatrix} \hat{V} & -\mathrm{i}c\hat{d}_z \\ -\mathrm{i}c\hat{d}_z & -2mc^2+\hat{V} \end{pmatrix} = \boldsymbol{A}^+, \tag{13}$$

$$\begin{aligned}\boldsymbol{B} &= \begin{pmatrix} 0 & -\mathrm{i}c\hat{d}_- \\ -\mathrm{i}c\hat{d}_- & 0 \end{pmatrix}\\ &= -\boldsymbol{B}^+\\ &= \begin{pmatrix} 0 & -\mathrm{i}c\hat{d}_+ \\ -\mathrm{i}c\hat{d}_+ & 0 \end{pmatrix}.\end{aligned} \tag{14}$$

That is, $\boldsymbol{A}$ is Hermitian and $\boldsymbol{B}$ is anti-Hermitian. For Kramer's partners, Dirac operator $\hat{h}_{\rm D}$ can be expressed as[16,17]

$$\hat{h}_{\rm D} = \boldsymbol{I}_2 \otimes \begin{pmatrix} \hat{V} & 0 \\ 0 & -2mc^2+\hat{V} \end{pmatrix} - c\check{i} \otimes \begin{pmatrix} 0 & \hat{d}_z \\ \hat{d}_z & 0 \end{pmatrix}$$

$$-c\check{j}\otimes\begin{pmatrix}0 & \hat{d}_y\\ \hat{d}_y & 0\end{pmatrix}-c\check{k}\otimes\begin{pmatrix}0 & \hat{d}_x\\ \hat{d}_x & 0\end{pmatrix}, \tag{15}$$

where $\hat{h}_{\rm D}$ is expressed as the quaternion, which exhibits the time reversal symmetry.

Quaternion algebra[18] was developed by Hamilton and Fresenius, however, the limited applications of quaternion in quantum mechanics have been made in recent years.

Quaternion is expressed as

$$q=\sum_{\lambda=0}^{3}V_\lambda e_\lambda=V_0+V_1\check{i}+V_2\check{j}+V_3\check{k}, \tag{16}$$

where

$$e_1=\check{i}\leftrightarrow \mathrm{i}\sigma_z;\ \ e_2=\check{j}\leftrightarrow \mathrm{i}\sigma_y;\ \ e_3=\check{k}\leftrightarrow \mathrm{i}\sigma_x. \tag{17}$$

Here, $\check{i}$, $\check{j}$, and $\check{k}$ are quaternion units, i is the imaginary unit, V_0, V_1, V_2, and V_3 are real part, σ_z, σ_y, and σ_x are Pauli spin matrices in Eq. (10). Quaternion includes a three-dimensional complex space and one-dimensional real space. It is known from Eq. (11) to Eq. (17) that quaternion algebra includes both time and space reversal symmetries, thus it is called the full symmetry group, and its matrix representation is called the co-representation. The $\hat{h}_{\rm D}$ in Eq. (15) is the Dirac operator of the full symmetry group. The Dirac equation can therefore be rewritten into a quaternion algebra form

$${}^q\hat{h}_{\rm D}{}^q\psi=E^q\psi. \tag{18}$$

3. Calculations of ground state for C_2, N_2, and O_2

The calculation is based on DIRRCI method of the full relativistic quantum mechanics with basis aug-cc-pVTZ-DK, and the results are listed in Table 1 and compared with the non-relativistic results obtained by the symmetry adapted cluster/configuration interaction (SAC-CI) method.[19]

Table 1. Energies, quadrupole moments and EFGs of molecules C_2, N_2, O_2, R_e/A^0 of ground state: $C_2(X^1\Sigma_g^+)$ 1.2425; N_2 $(X^1\Sigma_g^+)$ 1.09768); O_2 $(X^3\Sigma_g^-)$ 1.20752, a.u. is the abbreviation for the atomic unit.

	Full relativistic	Nonrelativistic	$\Delta E=E_{nr}-E_r$
C_2			
Energy ($r_e=1.2425$)	−75.433103564340826 a.u.	−75.400700534919793 a.u.	0.0324 a.u.
Quadrupole	$xx=yy=-6.86961$ a.u.	$xx=yy=-6.87162$ a.u.	
	$zz=13.7392$ a.u.	$zz=13.7432$ a.u.	
EFG/a.u.	nucleus: C	nucleus: C	
	$q_{xx}=q_{yy}=-0.41506$ a.u.	$q_{xx}=q_{yy}=-0.41544$ a.u.	
	$q_{zz}=0.83012$ a.u.	$q_{zz}=0.83090$ a.u.	
N_2			
Energy ($r_e=1.09768$)	−107.74751866684585	−107.68414603227684 a.u.	0.0634 a.u.
Quadrupole	$xx=XY=-21.2949$ a.u.	$xx=XY=-21.3074$ a.u.	
	$zz=42.5898$ a.u.	$zz=42.6149$ a.u.	
EFG/a.u.	nucleus: N	nucleus: N	
	$q_{xx}=q_{yy}=-0.891865$ a.u.	$q_{xx}=q_{yy}=-0.891620$ a.u.	
	$q_{zz}=1.78373$ a.u.	$q_{zz}=1.78324$ a.u.	
O_2			
Energy ($r_e=1.20752$)	−149.72173187768388 a.u.	−149.60879565740510	0.1129 a.u.
Quadrupole	$xx=yy=-10.524667$a.u.	$xx=yy=-10.527699$ a.u.	
	$zz=21.049334$ a.u.	$zz=21.055310$ a.u.	
EFG/a.u.			
	nucleus: O	nucleus: O	
	$q_{xx}=q_{yy}=-0.658832$ a.u.	$q_{xx}=q_{yy}=-0.658232$ a.u.	
	$q_{zz}=1.31766$ a.u.	$q_{zz}=1.316465$ a.u.	

Notice that EFG: 1 a.u. = 9.71736 E + 21 $\mathrm{V\cdot m^{-2}}$; Quadrupole: 1 a.u. = ea_0^2.

4. Charge distributions of quadrupole for molecules C_2, N_2, and O_2

The quadrupole is the second-rank tensor with two-dimensional charge distribution. As an example, the charge distribution of N_2 is given in detail as follows:

$$q_ze=\frac{42.58988\times e0.529177^2}{1.09768}=10.8650^e,$$
$$q_{x(y)}e=-\frac{21.2949\times e0.529177^2}{1.09768}=-5.4325e,$$

where e is the electron charge. Similarly, we also calculated the charge distributions for C_2 and O_2. The calculated results are all listed in Table 2. The quadrupole charge distribution of N_2 is plotted in Fig. 1. There are 10.8650 positive electron charges on the one of diagonal line, i.e. z axis of a quadrilateral, and 5.4325 negative electron charges on another diagonal line, i.e. x or y axis, that is, two-dimensional charge distribution. It is obvious that the quadrupole charge distribution of N_2 most deviates from equilibrium, for its many charges concentrate on its two sides, which is in agreement with the well-known characteristic of the nitrogen molecule.

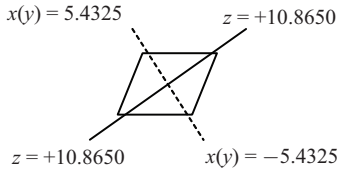


Fig. 1. Quadrupole charge distribution of N_2.

Table 2. Quadrupole charge distributions (QCDs) of C_2, N_2, and O_2.

	C_2/e	N_2/e	O_2/e
q_z	3.0965	10.8650	4.8803
$q_{x(y)}$	−1.5483	−5.4325	−2.4402

5. Electric field gradients[22] and second order force constants of molecules C_2, N_2, and O_2

EFGs at the positions of the nuclei in the molecules C_2, N_2, and O_2 are calculated using the full relativistic quantum mechanics. From Table 1, it is obvious that the general characteristics of EFGs for the symmetrical diatomic molecules are that their values of EFGs symmetrically descend around the z axis and ascend along the z axis; the latter should be of benefit to the formation of chemical bonds.

Suppose that the diatomic potential can be expressed as

$$V = \frac{1}{2}k_2(r-r_e)^2 + \frac{1}{6}k_3(r-r_e)^3 + \frac{1}{24}k_4(r-r_e)^4, \quad (19)$$

where r is the nuclear distance; r_e is its equilibrium nuclear distance; k_2, k_3, and k_4 are the quadratic, cubic, and quartic force constants, respectively. The negative derivative of potential with respect to bond distance r is the electric field force of the nucleus, therefore

$$qE = f = -\frac{\partial V}{\partial r} = k_2(r-r_e) + \frac{1}{2}k_3(r-r_e)^2 + \frac{1}{6}k_4(r-r_e)^3, \quad (20)$$

where E is the electric field strength and q is the electric charge. From Eq. (20) we can obtain the EFG $\partial E/\partial r$, and

$$q\frac{\partial E}{\partial r} = k_2 + k_3(r-r_e) + \frac{1}{2}k_4(r-r_e)^2. \quad (21)$$

If $r = r_e$, then the quadratic force constant k_2 will be

$$q\frac{\partial E}{\partial r} = q(EFG) = k_2. \quad (22)$$

Suppose that there is 1 a.u. of electric charge (negative) and at 1 a.u. of EFG, the quadratic force constant k_2 is as follows:

$$\begin{aligned} k_2 &= 1\ \text{a.u.(electron charge)} \times 1\ \text{a.u.(EFG)} \\ &= -4.8029\times10^{-10}(\text{CGSE}) \times 9.71736\times10^{21}\frac{V}{\text{m}^2} \\ &= -4.8029\times10^{-10}(\text{CGSE}) \times 9.71736\times10^{21} \\ &\quad \times \frac{\text{V}}{10^4\ \text{cm}} \times \frac{1}{300}(\text{CGSE})\frac{1}{\text{cm}} \\ &= 1.55717\times10^6\frac{\text{dyne}}{\text{cm}} = 1.55717\times10^6(\text{g}\cdot\text{s}^{-2}) \\ &= 1.55717\times10^6\frac{\text{g}\cdot\text{cm}^2\cdot\text{s}^{-2}}{\text{cm}^2} \\ &= 1.55717\times10^6\frac{\text{g}\cdot\text{cm}\cdot\text{s}^{-2}}{\text{cm}}\left(\frac{\text{dyne}}{\text{cm}}\right) \\ &= 1.55717\times10^6\left(\frac{\text{erg}}{\text{cm}^2}\right), \end{aligned} \quad (23)$$

where 1 V = CGSE/300.

There are two P electrons in each carbon atom. The quadratic force constants of C_2 can be calculated to be

$$\begin{aligned} k &= (0.8301211216/2 + 0.8301211216/2) \\ &\quad \times 1.55517\times10^6\left(\text{erg/cm}^2\right) \\ &= 12.9098\times10^5(\text{dyne/cm}) \end{aligned}$$

and the harmonic frequency to be

$$\begin{aligned} \omega &= \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \\ &= \frac{1}{2\times3.1416\times3\times10^{10}} \\ &\quad \times \left(\frac{1.29098\times10^6\times6.02\times10^{23}}{6}\right)^{1/2} \\ &= 0.01909327\times10^5 \\ &= 1909.327\ \text{cm}^{-1}. \end{aligned}$$

The above quantities of N_2 and O_2 are also calculated in a similar way. Their results are all listed in Table 3.

Table 3. Values of quadratic force constant (k) and harmonic frequency (ω) of C_2, N_2, and O_2 [unit: k ($\times10^5$ dyne/cm); ω (cm^{-1})].

	Present EFG data		Spectral data[20]	Potential data[21]
	k (Expt. R_e/A^0)	ω	ω	k (Cal. R_e/A^0)
C_2	12.9098(1.2425)	1909.327	1854.71	12.1608(1.2430)
N_2	18.4934(1.09768)	2115.5	2358.57	22.9482(1.0977)
O_2	10.24595(1.20752)	1473.32	1580.19	11.7660(1.2075)

6. Conclusions

Relying on the full relativistic quantum mechanics, we obtain reliable values of energy, quadrupole moment, and electric field gradient (EFG) of C_2, N_2, and O_2 molecules. The differences in energy between the relativistic and non-relativistic calculations are 0.0324, 0.0634, and 0.1129 a.u. for C_2, N_2, and O_2, respectively, that is, from C_2 to O_2, the relativistic effect is increased about 3.5 times. Therefore, even for the molecules consisting of the atoms from the same period in the periodic table, the relativistic effects are remarkably different.

The dipole charge distributions for these symmetrical molecules are all in equilibrium, however, the quadrupole charge distributions are far from equilibrium. Among them, there is the most remarkable deviation from equilibrium for N_2, for its many charges concentrate on two sides of the

molecules, which is in agreement with the well-known characteristic of the nitrogen molecule.

This is the first exploration that the force constant is essentially caused from electric field gradient, and indirectly related to spectroscopic data. It is proved that the quadratic force constant k_2 is the product of charge and EFG at its equilibrium nuclear distance. The quadratic force constants and harmonic frequencies derived from EFG are quite reasonable.

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