Ab initio SCF calculations on the potential energy surface of potassium cyanide (KCN)

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The potential energy surface of KCN has been generated by *ab initio* SCF calculations in the region of equilibrium bond distances. An analytic representation of the surface is presented. The calculations show that the bonding between K and CN is ionic, and that the structure of KCN is triangular, which confirms recent experimental findings. The computed geometry is $\angle KCN = 62.4°$, $r_{CK} = 5.492a_0$, and $r_{CN} = 2.186a_0$.

I. INTRODUCTION

Until recently not much was known about the geometry of the alkali cyanides. Experimental information was scarce and inconclusive, and quantum chemical calculations were confined to lithium cyanide.[1-3] These calculations indicated that the two possible linear structures LiCN and LiNC correspond to local minima on the potential energy surface, and that the surface is extremely flat in the angular coordinate describing the orbiting of the lithium atom around the cyanide. Furthermore, the depths of the two local minima are hardly different: recent MBPT (many body perturbation theory) studies[3] show that LiCN is more stable than LiNC by an amount of not more than 3.9 kcal/mole. Similarly, hydrogen cyanide is linear.[4,5] A recent experimental value[6] for the energy of the rearrangement HCN → HNC is + 10.3 kcal/mole, which is significantly smaller than a recent state-of-the-art *ab initio* value[3] of + 15 kcal/mode.

Very recent microwave and molecular beam electric resonance studies[7] have shed light on the structure of potassium cyanide (KCN). Somewhat unexpectedly the experiments show that KCN in contrast to HCN and LiCN, is triangular. From the inertial defect of the rotational spectrum the lowest vibrational transition energy can be estimated: $\omega = 157\ \mathrm{cm}^{-1}$.[7] This value is in fair agreement with the frequency 139 cm^{-1} measured for the bending mode of KCN trapped in solid argon.[8] Such a low bending frequency implies that KCN, just like LiCN, is a floppy molecule, or, more precisely, that the potential energy surface around the minimum is flat in the bending direction. With regard to nonrigidity, KCN lies between the class of triatomic van der Waals molecules such as $Ar-N_2$ ($\omega \approx 20\ \mathrm{cm}^{-1}$)[8] and the chemically bonded molecules such as, for example, SO_2($\omega = 517\ \mathrm{cm}^{-1}$).[9] It is therefore interesting to study the nuclear motion of the KCN molecule; to which end one needs—in the spirit of the Born–Oppenheimer approximation—a potential energy surface.

The subject of this paper is the *ab initio* computation and the subsequent analytic representation of the potential energy surface of KCN in the region of minimum energy. As we shall show below, the quantum chemical calculations predict a triangular structure for KCN, which is in good agreement with the geometry obtained from the rotational spectra. An additional advantage of the *ab initio* calculations is that it is an easy and straightforward matter—once the wave function is known—to calculate the electric field gradients at the ^{14}N and ^{39}K nuclei. These numbers are of great help in the interpretation of the rotational spectra in which many lines are split because of the coupling of the electrons with the nuclear quadrupole moments.

In order to obtain the energy surface with a grid fine enough to allow a reliable analytic representation, we had to restrict ourselves to LCAO–SCF (linear combination of atomic orbitals–self consistent field) calculations. Inclusion of correlation in a reliable manner, besides being costly, is unlikely to appreciably alter the shape of the surface in the bonding region. In order to explain this, we note that the small difference between the experimental ionization potential of the K atom, 4.339 eV,[10] and electron affinity of CN, 3.82 eV,[11] means that for the distance R from the center of mass of CN to K, less than about 53 bohr, the gain in Coulomb energy results in the transfer of an electron from K to CN. As we are only concerned with values of R in the range 4.5 to 8.0 bohr, we feel that for our purpose the assumption of complete charge transfer is fully justified. Further support for this premise will be provided by analysis of the calculated dipole moment and by the bond length of the cyanide anion.

So, the bonding in KCN is dominated by Coulombic attraction and exchange repulsion between closed-shell monomers. It is known from calculations on van der Waals molecules (see, for example, Ref. 12) that first order (electrostatic and exchange) interactions, as well as second order induction terms, are well described by the SCF method. The dominant induction term in this case is the monopole induced dipole interaction, which has an asymptotic R^{-4} dependence. The most important correlation energy contribution is in this case the dispersion interaction. This interaction has asymptotically as the leading term an R^{-6} term, which usually is fairly isotropic. So its influence on the shape of the potential energy surface is likely to be much smaller than the effect of the induction energy.

Summarizing, the SCF method may be expected to be suited for the ionically bound molecule KCN.

II. SCF CALCULATIONS

All LCAO–SCF calculations have been performed with an AO basis consisting of Cartesian GTO's (Gaussian type

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TABLE I. Some results for the cyanide anion.

	Present work	Literature
Energy at r_e	−92.338 547 a.u.	−92.346 796 a.u.[a]
r_e	2.186 a_0	2.186 a_0[a]
Affinity of CN	3.25 eV	3.29 eV[a]
$\alpha_{\parallel}$	27.2 a_0^3	30.0 a_0^3[b]
$\alpha_{\perp}$	17.7 a_0^3	20.0 a_0^3[b]
μ[c]	0.5467 D	−0.3749 D,[b,d] 0.811 D,[e] 0.3792 D[f]
Field gradient[g] at N	0.3467 esu	...

[a] Near Hartree–Fock value of Ref. 14.

[b] Reference 16.

[c] Polarity C^-–N^+, expressed with respect to center of mass of ^{12}C–^{14}N.

[d] We suspect the sign to be in error.

[e] R. Bonaccorsi, C. Petrongolo, E. Scrocco, and J. Tomasi, Chem. Phys. Lett. 3, 473 (1969).

[f] E. Clementi and D. Klint, J. Chem. Phys. 50, 4899 (1969).

[g] $-\left\langle \frac{3x^2-r^2}{r^5} \right\rangle$.

orbitals). Such a basis has to meet two obvious requirements in order to describe reliably the ionic bond in KCN: both the electron affinity of the CN radical and the ionization potential of the K atom must be reliably reproduced.

For cyanide, the basis of Wahlgren *et al.* [13] was chosen. On each of the atoms an extra diffuse *d* orbital was placed with $\alpha_C = 0.21$ and $\alpha_N = 0.32$, in order to improve the calculated polarizability of CN^-. This gives an (11*s*, 6*p*, 2*d*/6*s*, 3*p*, 2*d*) basis on both the carbon and the nitrogen atom. The bond distance of the free CN^-, optimized in this basis, is $r_e = 2.186$ bohr, which is the same as the near Hartree–Fock value of Ref. 14. Extensive correlation calculations give $r_e = 2.217$ bohr. [15] The vertical electron affinity, calculated as the total energy difference between the radical and the anion at $r = 2.186$ bohr in the present basis is 3.25 eV. The SCF limit is estimated at 3.29 eV[14]; the experimental adiabatic value lies at 3.82 eV. [11]

Another property of importance in the interaction between CN^- and K^+ is the dipole polarizability of the anion. Finite field SCF calculations on CN^- yield $\alpha_{\parallel} = 27.2 a_0^3$ and $\alpha_{\perp} = 17.7 a_0^3$. These and other properties of CN^- are summarized in Table I.

An adequate Gaussian basis for potassium is not readily available in the literature. For instance, the basis of Ref. 17 gives an ionization potential of −5.0 eV, which is of the wrong sign. This erroneous result is due to an overcontraction of the outer orbitals. A very large STO (Slater type orbital) basis gives 4.0 eV, [18] with the corresponding experimental figure being 4.39 eV. So the Hartree–Fock method is capable of giving a reasonable estimate of the ionization potential of the K atom. (Note that the values quoted here are differences in energy between the atom and the ion, not the energies of the 4*s* orbital.)

Being unable to find an adequate K basis, we decided to compose our own. To the optimized 1*s* orbital of Ref. 17, consisting of a contraction of six primitives, we added 15*s* and 15*p* orbitals. The exponents are equally spaced on a logarithmic scale (a geometric progression). After a number of trial calculations the inverval covered by the exponents was chosen to be $(10^{-2}, 10^3)$ bohr^{-2}. Since the *s* orbital with $\alpha = 1000$ fell in the same range as the 1*s* orbital, we removed it from the basis. After contraction, this basis gives as a first ionization potential the Hartree–Fock limit[18] value of 4.005 eV.

In order to give more flexibility to the basis in the valence region, we have added one 3*d* orbital to the K atom with $\alpha = 0.3354$, a value corresponding[19] to the optimal exponent $\zeta = 2.575$ of a 3*p*-STO of potassium. The final K(20*s*, 15*p*, 1*d*) basis has been contracted to a K[11*s*, 9*p*, 1*d*] basis and is given in Table II.

We will argue in Sec. III that to a good approximation KCN can be considered to be a dimer consisting of the two closed-shell monomers K^+ and CN^-. A very sensitive measure of the usefulness of monomer basis sets for dimer calculations is the basis set superposition error. This error is defined as the energy lowering of a monomer due to the extension of its basis by the orbitals on the other monomer. Calculation of this error at the geometry $R = 5.04$ bohr and $\vartheta = 90°$ (see Fig 1 for the definition of the coordinates), which is near the experimental structure, yields 0.0017 hartree for CN^- or 1% of the SCF interaction energy. There is imperceptible energy lowering of K^+ due to the CN basis. Because this basis set superposition error is small, we decided not to correct for it in the subsequent calculations.

Next we considered whether the CN^- bond distance was much affected by the presence of the K^+ ion. So, at $R = 5.0$ bohr and $\vartheta = 90°$ we optimized the CN^- bond length, finding $r_e = 2.180$ bohr. The small change in distance of 0.006 bohr reinforces our belief that KCN may be looked upon as a van der Waals molecule consisting of ionic monomers. Because of the small variation in distance, we did not think it worthwhile to vary the CN^- bond length and have kept it fixed at 2.186 bohr in all ensuing calculations. So, when we speak in this paper of the potential energy surface of KCN, we really mean a function on the manifold of constant r_{CN} and variable R and ϑ.

The actual dimer calculations were conducted in two stages. First we made an exploratory scan of the surface, finding only one minimum at a geometry not far from the experimental triangularly shaped structure. [7] This exploratory scan consisted of 25 points. On basis of the insight thus obtained we proceeded more systematically in the second stage of the calculations. We picked the points dictated by the Gauss–Legnedre quadrature scheme, which, as will be explained below, leads to an expansion of the interaction in terms of Legendre polynomials with R dependent coefficients. This analytic fit required 24 more points on the poten-

TABLE II. Gaussian basis for potassium.

Type	Exponent	Contraction coefficient
s	554 579.0	0.000 399
	81 718.1	0.003 131
	18 358.1	0.016 838
	5 026.74	0.074 591
	1 604.67	0.258 715
	594.069	0.721 776
s	439.40	0.031 544
	193.07	0.269 907
	84.834	0.354 755
s	37.276	1.0
s	16.380	0.065 188
	7.196 8	0.559 933
s	3.162 2	1.0
s	1.389 5	0.175 385
	0.610 54	0.696 494
s	0.268 27	1.0
s	0.117 88	1.0
s	0.051 795	1.0
s	0.022 758	1.0
s	0.010 000	1.0
p	1 000.0	0.001 412
	439.40	0.002 874
	193.07	0.014 365
	84.834	0.046 923
p	37.276	0.141 853
	16.380	0.305 673
	7.196 8	0.418 794
p	3.162 2	1.0
p	1.389 5	1.0
p	0.610 54	0.489 323
	0.268 27	0.318 949
p	0.117 88	1.0
p	0.051 795	1.0
p	0.022 758	1.0
p	0.01	1.0
d	0.335 4	1.0

$E = -599.134\,241\,41$ a.u.
Ionization potential 4.005 eV
$\alpha(\mathrm{K}) = 415.\,a_0^3$
$\alpha(\mathrm{K}^+) = 4.86\,a_0^3$

tial energy surface.

All calculations have been performed with the ATMOL 3 suite of programs.[20] Each point calculated with the present 98-dimensional basis took about 3 h integration—and 3 h SCF—time on an IBM 370/158.

III. THE BONDING IN KCN

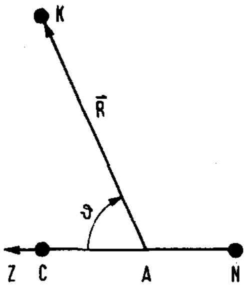

FIG. 1. Coordinate system for KCN. A denotes the center of nuclear mass of ^{12}C–^{14}N.

The ionicity of KCN referred to in the Introduction is confirmed by the analysis of the dipole moment given in Table III. The polarization entries in Table III are obtained by solving the SCF equations for CN^- and K^+ in the presence of a positive and a negative unit charge, respectively, at the position of the other monomer. In order that the decomposition, given in Table III, makes any sense at all, the basis set superposition errors in the dipole moment must be small. At $R = 5.04$ bohr this error is 1.0%, while at $R = 8.0$ bohr it is 0.51% of the y component of the SCF dipole, pointing from CN^- to K^+.

From Table III, it follows that the transfer of a unit charge and the subsequent polarizations account for about 98% of the SCF dipole moment. The difference of ~2% can be attributed to exchange effects and incomplete charge transfer. Note the sign change in the difference between $R = 5.04$ and 8.0 bohr, indicating that indeed two effects are operative. The analysis of many other geometries shows that charge transfer and polarization account for over 90% of the dipole moment everywhere in the bonding region. The largest deviations are found where there is appreciable exchange.

Once it has been established that KCN may be considered a dimer consisting of two closed shell ions, the theory commonly applied to van der Waals molecules[12] becomes applicable. First, we take the Hartree–Fock energies of the separate ions K^+ and CN^- as our energy zero. Secondly, we separate the interaction into a long range part, which is described by RSPT (Rayleigh–Schrödinger perturbation theory) and a short range part, which in our case is defined as the difference of the SCF and long range interactions. If one neglects dispersion

TABLE III. Decompositon of KCN dipole[a] for $\vartheta = 90°$.

	$R = 5.04$	$R = 8.0$
Polarization K^+	−0.1479	−0.0756
Polarization CN^-	−0.6636	−0.2734
eR	5.0400	8.0000
Total	4.2285	7.6510
SCF	4.3289	7.5454
Difference	2.3%	1.4%

[a] Component pointing from center of mass of ^{12}C–^{14}N towards K^+ expressed in a.u.

interactions and also temporarily the polarizations of the K^+ ion, one may invoke the Laplace expansion[21] for $1/r_{12}$ and write the interaction Hamiltonian V^{AB} (A is CN^-, B is K^+) as

$$V^{AB}=\sum_{l=0}^{\infty} R^{-l-1} \sum_{m=-l}^{l} (-1)^m Q_{lm}^{A} C_{l,-m}(\hat{R}) , \qquad (1)$$

instead of in the form of the more complicated multipole expansion.[22] In Eq. (1) $\mathbf{R}=(R,\hat{R})$ is the position vector of B expressed in polar coordinates, $C_{l,m}(\hat{R})$ is a spherical harmonic in Racah's normalization,[23] and Q_{lm}^{A} is the operator[12] representing the multipole moment of order l on A. Note that in Eq. (1) the assumption has been made that $\mathbf{R}$ is longer than any of the position vectors of the particles of A. This condition means that Eq. (1) is only applicable for cases where the differential overlap between the charge cloud of A and the point charge B is negligible.

Inserting the expansion (1) into the RSPT first order energy expression, denoted by $E^{(1)}$, we obtain a series in R^{-1}, with the kth term representing the electrostatic interaction of the unit charge B with the 2^l pole $\langle Q_{lm}^{A}\rangle$, $m=-l,\dots,l$, on A. Proceeding similarly for the second order RSPT energy $E_A^{(2)}$ and expanding the product $C_{l_1m_2}(\hat{R})C_{l_2m_2}(\hat{R})$ in a Gaunt series[24] one obtains

$$E_A^{(2)}=-\frac{1}{2}\sum_{l_1,l_2=0}^{\infty} R_B^{-l_1-l_2-2} \sum_{m_1=-l_1}^{l_1}\sum_{m_2=-l_2}^{l_2} \times\sum_{L}(-1)^M C_{L,-M}(\hat{R}) G(LM|l_1m_1;l_2m_2)\alpha_{m_1m_2}^{l_1l_2} . \qquad (2)$$

Here

$$\alpha_{m_1m_2}^{l_1l_2}:=2{\sum_n}' \frac{\langle 0|Q_{l_1m_1}^{A}|n\rangle\langle n|Q_{l_2m_2}^{A}|0\rangle}{E_n-E_0} \qquad (3)$$

is the (m_1,m_2) component of the polarizability tensor of order (l_1,l_2). The Gaunt coefficient, expressed in terms of Wigner $3jm$ symbols, is[22]

$$G(LM|l_1m_1;l_2m_2):=(2L+1)\begin{pmatrix} l_1 & l_2 & L\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l_1 & l_2 & L\\ m_1 & m_2 & M\end{pmatrix} . \qquad (4)$$

Classically, $E_A^{(2)}$ is the energy associated with the polarization of the charge distribution A by the field of the point charge B.

For the present case of a linear molecule A in a Σ state, the expressions for $E^{(1)}$ and $E_A^{(2)}$ may be simplified by choosing the z axis along the molecular axis and B in the xz plane. Further we choose the origin at the center of mass of A($=CN^-$) (cf. Fig. 1). One then easily derives[25] the following expression in terms of Legendre polynomials $P_L(x)$, $x=\cos\vartheta$,

$$E^{(1)}=\sum_{L=0}^{\infty} R^{-L-1}P_L(x)\langle Q_{L0}^{A}\rangle , \qquad (5)$$

$$E_A^{(2)}=\sum_{l_1 l_2=0}^{\infty} R^{-l_1-l_2-2}\sum_L P_L(x)C_{l_1l_2L}^{A} , \qquad (6)$$

where the induction coefficients are

$$C_{l_1l_2L}^{A}:=-\frac{1}{2}\sum_{m=0}^{\min(l_1l_2)}(2-\delta_{m0})(-1)^m \times G(L0|l_1m;l_2-m)\tilde{\alpha}_{m_1m_2}^{l_1l_2} . \qquad (7)$$

The polarizability tensor $\tilde{\alpha}_{m_1m_2}^{l_1l_2}$ is the same as that defined in Eq. (3), but expressed in terms of tesseral (real) harmonics, which is more convenient for computer applications.

The calculated values for $\langle Q_{L0}^{A}\rangle$ and $C_{l_1l_2L}^{A}$ ($A=CN^-$) are given in Table IV. Excepting the case $l_1=l_2=1$, which is based on a finite field SCF polarizability, all induction coefficients are computed from second-order (uncoupled) Hartree–Fock polarizabilities,[26] obtained from the program MULTPROP.[27]

The only polarization of K^+ by CN^- of any significance is the ordinary dipole induction

$$E_B^{(2)}=-\tfrac{1}{2}\alpha^B R^{-4} , \qquad (8)$$

which is isotropic [multiplies $P_0(x)=1$]. The (finite field (SCF) polarizability α^B of K^+ is $4.86a_0^3$.

In Fig. 2 the total long range energy $E^{(1)}+E_A^{(2)}+E_B^{(2)}$ is depicted as a function of ϑ (cf. Fig. 1). R is here the computed equilibrium value of 5.055 bohr. The long range energy has local minima for the two linear structures. The minimum of KCN is deeper than of KNC, which is because the dipole moment of CN^- (expressed with respect to its center of mass) points from carbon to nitrogen. It could loosely be stated that most of the extra electron of CN^- is on the carbon atom, for the CN radical has a dipole moment of opposite sign.

This idea, of the excess charge being mainly accu-

TABLE IV. Long range coefficients[a] (in a.u.) for CN^- in field of positive unit charge [cf. Eqs. (5) and (6)].

	0	1	2	3	4	5	6
$\langle Q_{LO}\rangle$	−1.000	−0.2151	−3.414	−3.819	−15.84	−14.29	−43.82
C_{11L}	−10.43 −(12.86)[b]		−3.17				
C_{21L}		−7.23		+2.03			
C_{22L}	−57.49		−35.71		5.23		
C_{31L}			−35.56		5.95		
C_{32L}		−101.45		−37.62		−14.23	
C_{33L}	−458.2		−353.7		−112.6		−108.3

[a] Expressed with respect to the system of axes in Fig. 1.

[b] $+K^+$.

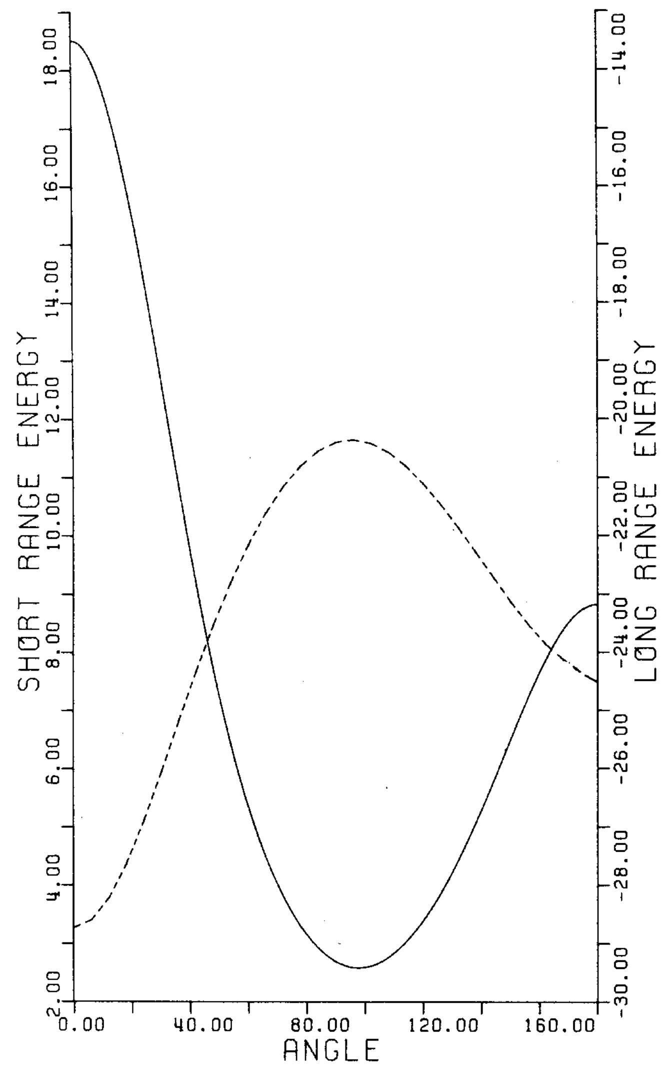

FIG. 2. Short range energy (full line) and long range energy (dashed line) as a function of the angle ϑ. $R=5.055$ bohr. Units: 10^{-2} hartree.

mulated on the carbon side, is further supported by the large exchange repulsion on that side. Figure 2 shows that the short range energy, which is dominantly exchange, is strongly repulsive for K$^+$ approaching towards the carbon, and that there is a deep minimum in between the carbon and the nitrogen atoms. This minimum predominates and hence the structure of minimum energy will be triangular.

Summarizing, one could qualitatively explain the triangular structure of KCN by the following reasoning: the dominant and isotropic Coulomb force (the first term in $E^{(1)}$) pulls K$^+$ towards the center of mass of CN$^-$. The exchange repulsion, keeping the ions apart, is least effective in between the carbon and the nitrogen atom. There the shortest distance between the ions is possible and the gain in Coulomb energy is maximized.

However, this simple rationalization cannot be the complete truth, because by similar reasoning one would predict all alkalicyanides to be triangular and LiCN is known to be linear.[1,2] So, the other bonding effects discussed in this section must be taken into account—as must be the possibility of incomplete charge transfer—in comparing different alkalicyanides.

IV. THE POTENTIAL ENERGY SURFACE OF KCN

In this section an analytic fit of the potential energy surface will be presented in the region of R values of minimum energy, ϑ varying between 0 and π, and r_{CN} kept constant at 2.186 bohr. The main purpose of this analytic representation is to facilitate the computation of the rotational and vibrational spectrum of KCN in its electronic ground state.[28]

In the previous section the long range interaction energy of K$^+$ and CN$^-$ has been expanded in terms of Legendre polynomials. It is convenient to have a similar expansion for the overlap dependent short range energy E_{SR}, which we define as the difference between the SCF energy and the long range energy given by Eqs. (5), (6), and (8) and by the values in Table IV. At this point we should emphasize that the fitted surface reproduces the total SCF potential. The separation into short and long range terms is done because the form of the long range interaction, and more particularly its R dependence, is known analytically. Furthermore, the fit is improved by removing the bulk of the attraction from the SCF interaction. Imperfections and omission in the long range coefficients are covered by the parameters of the short range potential.

There is no theory relating the short range energy to properties of the individual monomers, which is understandable as the exchange repulsion is caused by the fact that the monomers cease to be identifiable for shorter distances. So we have to invoke numerical techniques to obtain the coefficients in the expansion

$$E_{\text{SR}}(R,x)=\sum_{L=0}^{N} D_L^{\text{SR}}(R)P_L(x)\,, \tag{9}$$

where $x:=\cos\vartheta$. Because Legendre polynomials are complete on the interval $[-1,1]^{29}$ the expansion is exact for N large enough, (N may be infinite). Since the polynomials are orthogonal one can write

TABLE V. Short range parameters KCN (in a.u.) [cf. Eqs. (9) and (11)].

	0	1	2	3	4	5	6
A_L^{SR}	−3.321	−0.6319	−4.644	−0.4427	−4.299	−4.583	−12.026
H_L^{SR}	0.8446	0.4613	1.387	0.5639	1.809	2.630	5.449
C_L^{SR}	0.07622	0.06908	0.01394	0.07245	−0.02183	−0.1135	−0.3625

TABLE VI. Structure of equilibrium KCN (in a.u.).

	This work	Experiment[a]	Difference
r_{ck}	5.492	5.145	6.3%
r_{cn}	2.186	2.213	1.2%
r_{kn}	4.880	4.812	1.4%
<KCN	62.4°	68.9°	9.4%
ϑ[b]	105.7°	97.8°	7.5%
R[b]	5.055	4.845	4.2%

[a] Reference 32, vibrationally averaged values.
[b] Defined in Fig. 1.

$$D_L^{SR}(R)=\frac{2L+1}{2}\int_{-1}^{1}E_{SR}(R,x)P_L(x)\,dx\,. \tag{10}$$

Following Ref. 30 we apply the Gauss–Legendre quadrature scheme to the evaluation of the integral in Eq. (10). It is a well-known property of the Gauss quadrature[31] that $(N+L+1)/2$ integration points are needed to do the integral (10) exactly. [Recall that by Eq. (9), N is the order of E_{SR}]. So, in our case we need $N+1$ quadrature points to obtain all $N+1$ expansion coefficients D_L^{SR} exactly.

From our exploratory set of calculations of the potential energy surface we know that the R values of minimum energy are between 5.0 and 6.2 bohr for different angles. Therefore we started the second set of calculations, aimed at the evaluation of $D_L^{SR}(R)$, at $R=4.5$ bohr, a short distance inside the repulsive region. We took a grid of ten angular points which we judged from our preliminary calculations to be more than sufficient, and indeed we found that the series (9) had converged at $N=6$. Consequently, we took seven quadrature points for the subsequent calculations at $R=5.0$ and 5.5 bohr.

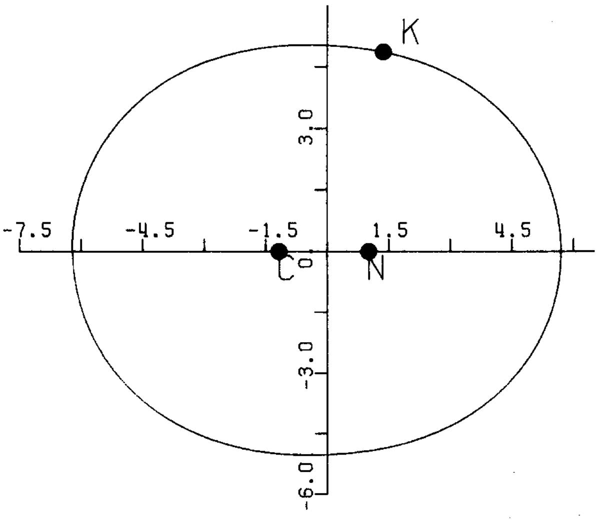

FIG. 3. The R values of minimum energy as a function of ϑ plotted in a polar graph. Units: bohr. The equilibrium structure of KCN is shown.

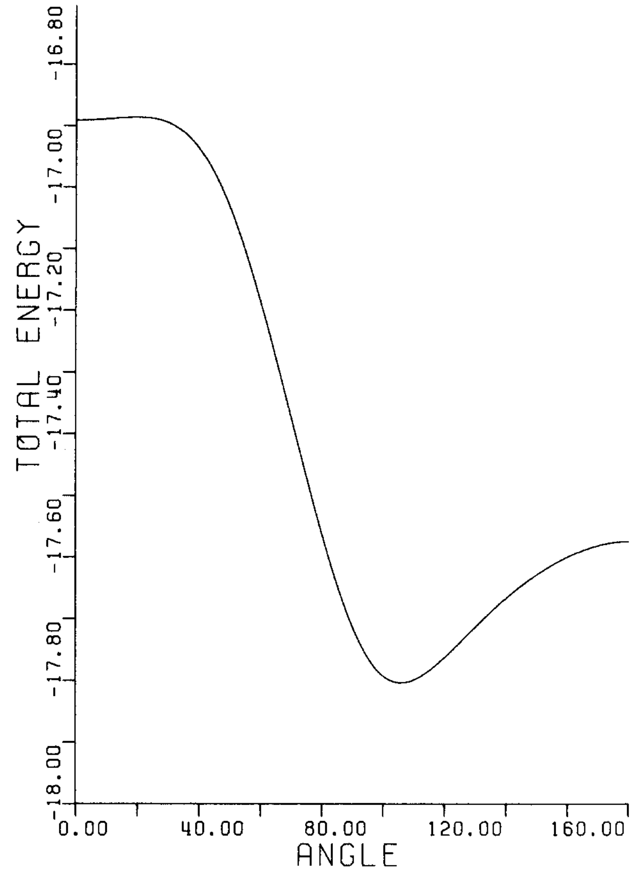

FIG. 4. Minimum of total energy (10^{-2} hartree) as a function of ϑ.

Having obtained $D_L^{SR}(R)$ at three different R values, we represented the results by

$$D_L^{SR}(R)=\exp(-A_L^{SR}-B_L^{SR}R-C_L^{SR}R^2)\,, \tag{11}$$

which is possible because all D_L^{SR} values are positive. The parameters A_L^{SR}, B_L^{SR}, and C_L^{SR}, obtained by a least squares polynomial fit of $\ln(D_L^{SR})$, are listed in Table V.

A note of warning must be given with regard to the applicability of the values in this table. Namely, the coefficients C_4^{SR}, C_5^{SR}, and C_6^{SR} are negative, which means that D_4^{SR}, D_5^{SR}, and D_6^{SR} go through a minimum and then tend to infinity for large R. The validity of Eq. (11) will not stretch much beyond the minima, the shortest of which arises for D_6^{SR} at $R=7.52$ bohr. However, at this distance the short range contribution to the interaction is already less than 1% of the long range contribution.

So, in the range of interest for the nuclear motion problem, the fit of the surface is excellent. Comparing the fitted values of the total interaction energy with the 25 SCF points in the first set of calculations, we find a mean deviation of 0.36%, with a largest error of 1.4% occurring at $\vartheta=90°$ and $R=8.0$ bohr.

V. DISCUSSION

By application of the analytic form of the potential energy surface obtained in the previous section, the

TABLE VII. Properties (in a.u.) of KCN in its computed equilibrium geometry. Molecule in *xz* plane, *C* atom on positive *z* axis. (cf. Fig. 1)

Energy	−691.505 399
Dipole moment	
$\langle z\rangle$	−1.288 3
$\langle x\rangle$	4.185 6
Quadrupole moment[a]	
$\frac{1}{2}\langle 3z^2-r^2\rangle$	−12.048
$\frac{1}{2}\langle 3x^2-r^2\rangle$	22.122
$\frac{1}{2}\langle 3y^2-r^2\rangle$	−10.074
$\frac{1}{2}\langle 3zx\rangle$	−9.287
Field gradient at N	
$-\langle(3z^2-r^2)/r^5\rangle$	1.021 9
$-\langle(3x^2-r^2)/r^5\rangle$	−0.523 3
$-\langle(3y^2-r^2)/r^5\rangle$	−0.498 6
$-\langle 3zx/r^5\rangle$	−0.007 6
Field gradient at K	
$-\langle(3z^2-r^2)/r^5\rangle$	−0.176 9
$-\langle(3x^2-r^2)/r^5\rangle$	0.389 6
$-\langle(3y^2-r^2)/r^5\rangle$	−0.212 9
$-\langle 3zx/r^5\rangle$	−0.109 7
Comparison with experiment[b]	
Field gradient at N[c]	
G_{aa}	−0.490 (−0.494)
G_{bb}	0.989 (1.043)
G_{cc}	−0.499 (−0.549)
Field gradient at K[d]	
G_{aa}	0.409 (0.426)
G_{bb}	−0.196 (−0.197)
G_{cc}	−0.213 (−0.228)

[a] With respect to center of mass of $^{12}C-^{14}N$.

[b] Experimental results (in brackets) from Ref. 32. Diagonal elements of field gradient tensor expressed with respect to principal axes of inertia tensor of $^{39}K-^{12}C-^{14}N$ in its experimental geometry.

[c] Nuclear quadrupole moment of ^{14}N: 0.0166 b from R. Bonaccorsi, E. Scrocco, and J. Tomasi, J. Chem. Phys. 50, 2940 (1969).

[d] Nuclear quadrupole moment of ^{39}K: 0.056 b, from R. W. Schmieder, A. Lurio, W. Happer, and A. Khadjavi, Phys. Rev. A 2, 1216 (1970).

geometry of minimum energy is determined and compared in Table VI with a very recent experimental microwave structure.[32] The agreement is very good and firmly establishes that KCN is triangular.

It is noteworthy that all computed intermonomer distances are too long. This could be due to the neglect of dispersion or to an underestimate of the polarizabilities by the present AO basis. Our Hartree–Fock CN^- bond distance, on the other hand, is slightly too short. The experimental bond distance of CN in KCN is very close to the high quality theoretical value of 2.217 bohr,[15] recently computed for the free CN^- anion. This confirms our finding that the bond distance is hardly affected by the presence of the potassium ion.

In Fig. 3 the minimum value of R is plotted as a function of ϑ in a polar graph. The path of minimum energy thus obtained is surprisingly symmetric, with a symmetry axis intersecting the CN^- bond at −0.267 bohr. However, the energy along the path, shown in Fig. 4, is not symmetric at all. In this figure one clearly sees illustrated the preference of KCN for a triangular geometry. One also sees that KNC has a lower energy than KCN, which is caused by the closer contact of the ions on the nitrogen side.

In Table VII some properties computed for the structure of minimum energy are given. Note that the agreement between the computed and the measured field gradients at the position of the K and the N nucleus is very good.

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[1] B. Bak, E. Clementi, and R. N. Kortzeborn, J. Chem. Phys. 52, 764 (1970).

[2] E. Clementi, H. Kistenmacher, and H. Popkie, J. Chem. Phys. 58, 2460 (1973).

[3] L. T. Redmon, G. D. Purvis, and R. J. Bartlett, J. Chem. Phys. 72, 986 (1980).

[4] J. W. Simmons, W. E. Anderson, and W. Gordy, Phys. Rev. 77, 77 (1950).

[5] R. A. Creswell, E. F. Pearson, M. Winnewisser, and G. Winnewisser, Z. Naturforsch. Teil A 31, 221 (1976).

[6] A. G. Maki and R. L. Sams quoted in Ref. 3.

[7] T. Törring, J. P. Bekooy, W. L. Meerts, J. Hoeft, E. Tiemann, and A. Dymanus, J. Chem. Phys. 73, 4875 (1980).

[8] G. Henderson and G. E. Ewing, Mol. Phys. 27, 903 (1974).

[9] G. Herzberg, *Molecular Spectra and Molecular Structure* III (Van Nostrand Reinhold, New York, 1966), p. 605.

[10] *Handbook of Chemistry and Physics*, 58th ed. (Chemical Rubber, Cleveland, 1977), p. E-68.

[11] J. Berkowitz, W. A. Chupka, and T. A. Walter, J. Chem. Phys. 50, 1497 (1969).

[12] A. van der Avoird, P. E. S. Wormer, F. Mulder, and R. M. Berns, Top. Curr. Chem. 93, 1 (1980).

[13] U. Wahlgren, J. Pacansky, and P. S. Bagus, J. Chem. Phys. 63, 2874 (1975).

[14] J. Pacansky and B. Liu, J. Chem. Phys. 66, 4818 (1977).

[15] P. R. Taylor, G. B. Bacskay, N. S. Hush, and A. C. Hurley, J. Chem. Phys. 70, 4481 (1979).

[16] J. E. Gready, G. B. Bacskay, and N. S. Hush, Chem. Phys. 31, 467 (1978).

[17] H. Kistenmacher, H. Popkie, and E . Clementi, J. Chem. Phys. 58, 1689 (1973).

[18] E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 178 (1974).

[19] R. F. Stewart, J. Chem. Phys. 52, 431 (1970).

[20] V. R. Saunders and M. F. Guest of the Daresbury Laboratory, Warrington, England. We wish to thank Dr. Guest for making the program available.

[21] E. U. Condon, G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, 1935).

[22] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83**, 628 (1951).

[23] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* 2nd ed. (Princeton University, Princeton, 1960).

[24] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, *The 3j and 6j symbols* (MIT, Cambridge, Mass., 1959).

[25] F. Mulder, A. van der Avoird, and P. E. S. Wormer, Mol. Phys. **37**, 159 (1979).

[26] F. Mulder, thesis, University of Nijmegen, The Netherlands, 1978.

[27] F. Mulder and R. M. Berns, Institute of Theoretical Chemistry, University of Nijmegen, The Netherlands.

[28] Work on the nuclear motion of KCN is in progress in this institute, in collaboration with Dr. B. T. Sutcliffe.

[29] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953), Vol. I.

[30] R. M. Berns and A. van der Avoird, J. Chem. Phys. **72**, 6107 (1980).

[32] J. Stoer, *Einführung in die Numrische Mathematik I* (Springer, Berlin, 1979).

[32] J. J. van Vaals and W. L. Meerts (to be published).