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Are Linear Molecules Really Linear ?
II. Re-interpretation of experimental B_0-values.

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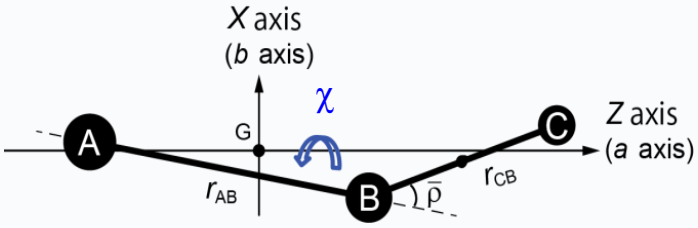
In the preceding talk (TH02), we demonstrated:

Any triatomic linear molecule will be observed as being "bent"
on ro-vibrationally average in any ro-vibronic state. $\langle\bar{\rho}\rangle > 0$



We characterize Nature through observation:

Theoretical → Calculation of expectation value, and we got $\langle\bar{\rho}\rangle > 0$

Experimental → B_0 from spectroscopy, corresponds also to bent structure???

However,
conventionally, structure parameters have been derived from exp. B_0's with the assumption $\langle\bar{\rho}\rangle = 0$.

Misbehaving results were obtained with $\langle\bar{\rho}\rangle = 0$:
for r_0 structure determined from two B_0's.

$B_0 \rightarrow r_0$ Winnewisser *et al*. (Tab. 1 Winnewisser et al, *J. Mol. Spec*., **39**, 149 (1971))

	HCN	$H^{13}CN$	$HC^{15}N$	DCN	$D^{13}CN$
$H^{13}CN$	1.06754(10) 1.15582(2)				
$HC^{15}N$	1.07703(20) 1.15395(4)	1.06017(35) 1.15720(7)			
DCN	1.062407(0) 1.156827(0)	1.062692(6) 1.156728(2)	1.062774(5) 1,156700(2)		
$D^{13}CN$	1.062086(8) 1.156889(2)	1.062416(13) 1.15678(4)	1.062496(14) 1.156754(4)	1.06585(9) 1.15564(3)	
$DC^{15}N$	1.061930(8) 1.156920(2)	1.062256(13) 1.156810(4)	1.062327(13) 1.156786(4)	1.07249(16) 1.15335(6)	1.05837(36) 1.15812(12)

$\Longrightarrow$ Δr
Black: r(H(D)-C) 0.01 Å
Blue: r(C≡N) 0.002 Å

Born-Oppenheimer approximation does not hold ? No!

Shrinkage parameter? NO !

They could not find the answer !

(Then, r_s, r_z, r_m, $r_m^{(2)}$ methods were presented.)

Now we start:

Re-interpretation of Experimentally reported B_0 value,
with $\langle\bar{\rho}\rangle$ as a variable.

Conventionally, $\langle\bar{\rho}\rangle = 0$ is assumed.

We will discuss r_0 structure of three-atom linear molecule.

Deriving geometrical parameters from experimental B_0 values

For a three-atom molecule, zero-point, averaged structure can be described with three structure parameters (r_{12}, r_{23}, $\bar{\rho}$) .

⇩

When we have more than three B_0's, we can determine $r_{12}^{(0)}$, $r_{23}^{(0)}$, $\bar{\rho}^{(0)}$.

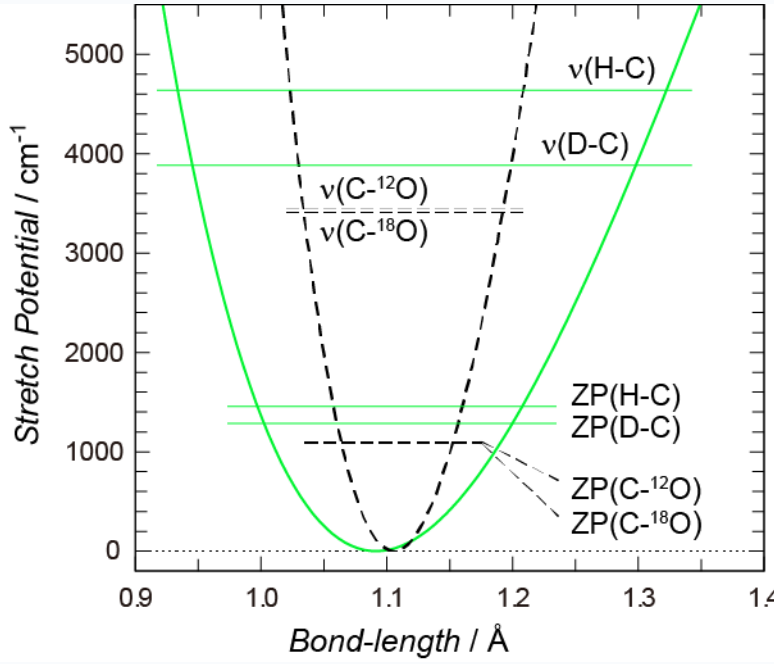
We should note, however;

1）Beforehand, the possibility of a set of geometrical parameters in common should be checked for the isotopologues. → Difficult to know by experiment

Amplitudes of stretching vibration are quite different for H—C and D—C bonds. Should be treated in separate groups !

（Difference in Anhamonicity effects is large.)

H-CO$^+$ vs D-CO$^+$ →



2) $\bar{\rho}^{(0)}$ should be treated as a variable.

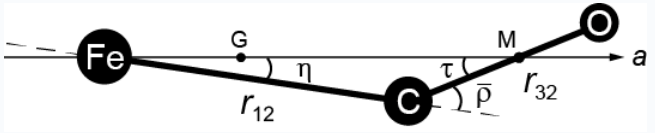
$^3\Sigma^-$ FeCO

- We have determined very accurate *ab initio* 3D PES.
- K. Tanaka *et al*., provided very accurate B_0's for 5 isotopologues (1997).

K. Tanaka, et al., *J. Chem. Phys*. 106 (1997) 2118.

How accurate our 3D PES ? B_0 from term-value spacing (DVR3D)

	B^0_{eff} / MHz		
	Exp. (Tanaka, *et al*.)	Calc.	%Deviation
$^{56}Fe^{12}C^{16}O$	4364.266(55)	4365.4	0.027
$^{54}Fe^{12}C^{16}O$	4413.94(29)	4414.9	0.022
$^{57}Fe^{12}C^{16}O$	4340.77(60)	4341.9	0.026
$^{56}Fe^{13}C^{16}O$	4332.28(8)	4333.4	0.026
$^{56}Fe^{13}C^{18}O$	4039.75(14)	4040.6	0.022



1) A set of common structure parameters ? Yes (DVR3D).

	$\langle r(\text{Fe-C})\rangle_0$ / Å	$\langle r(\text{C-O})\rangle_0$ /Å	$\langle\bar{\rho}\rangle_0$ /deg.	$\langle\tau\rangle_0$	B_0 /MHz	%Deviation
$^{56}Fe^{12}C^{16}O$	1.7303	1.1631	7.40 (3.6)	5.349	4360.9	-0.08
$^{54}Fe^{12}C^{16}O$	1.7303	1.1631	7.40 (3.6)	5.350	4410.3	-0.08
$^{57}Fe^{12}C^{16}O$	1.7303	1.1631	7.40(3.6)	5.348	4337.4	-0.08
$^{56}Fe^{13}C^{16}O$	1.7302	1.1631	7.30(3.5)	5.320	4328.9	-0.08
$^{56}Fe^{13}C^{18}O$	1.7301	1.1629	7.25 (3.5)	5.219	4036.4	-0.08

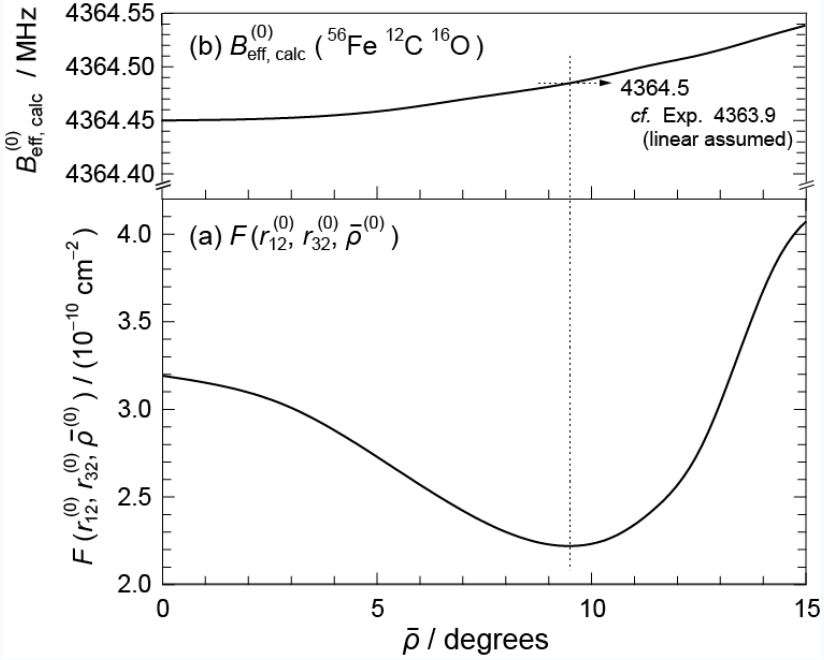
2) Least Squares Fitting (LSQ) using Experimental B_0's (Tanaka *et al*. (1997), IR), for a given initial guess $\left(r_{12}^{(0)}, r_{32}^{(0)}, \bar{\rho}^{(0)}\right)$

$$F\left(r_{12}^{(0)}, r_{32}^{(0)}, \bar{\rho}^{(0)}\right) = \sum_i \left(B_{0,\mathrm{exp}} - B_{\mathrm{eff,calc}}^{(0)}\right)_i^2$$

$$(i = {}^{56}\mathrm{Fe}^{12}\mathrm{C}^{16}\mathrm{O},\ {}^{54}\mathrm{Fe}^{12}\mathrm{C}^{16}\mathrm{O},\ {}^{57}\mathrm{Fe}^{12}\mathrm{C}^{16}\mathrm{O},\ {}^{56}\mathrm{Fe}^{13}\mathrm{C}^{16}\mathrm{O},\ {}^{56}\mathrm{Fe}^{13}\mathrm{C}^{18}\mathrm{O})$$

$$B_{\mathrm{eff,calc}}^{(0)} = \frac{h}{8\pi^2 c}\left[\frac{1}{2}\left(\frac{1}{I_{bb}\left(r_{12}^{(0)}, r_{32}^{(0)}, \bar{\rho}^{(0)}\right)} + \frac{1}{I_{cc}\left(r_{12}^{(0)}, r_{32}^{(0)}, \bar{\rho}^{(0)}\right)}\right)\right]$$

I_{kk}: Moment of inertia for kk principal axis



⟹ Exp. B_0 corresponds to a Bent structure of 9.48°

cf. $\langle\bar{\rho}\rangle_0 = 7.4°$

When $\langle\bar{\rho}\rangle_0 = 0$ is assumed, we obtain Bond-length projected onto *a*-axis.

⟹ r(Fe-C) = 1.7268 Å, r(C-O) = 1.1606

cf. $\langle r(\mathrm{Fe\text{-}C})\rangle_{0,\mathrm{proj}} = 1.7287$ Å, $\langle r(\mathrm{C\text{-}O})\rangle_{0,\mathrm{proj}} = 1.1589$ Å

$^1\Sigma^+$ HCO^+

Least-Squares Fit (LSQ) of Exp. B_0 values

3 roots for 3 B_0's

r(H-C)	r(C-O)	$\bar{\rho}$	→	B_0 (for H-^{12}C-^{16}O$^+$)
1.1162	1.1076	12.45°		44594.42

r(D-C)	r(C-O)	$\bar{\rho}$	→	B_0 (for D-^{12}C-^{16}O$^+$)
1.1064	1.1073	9.77°		36019.68

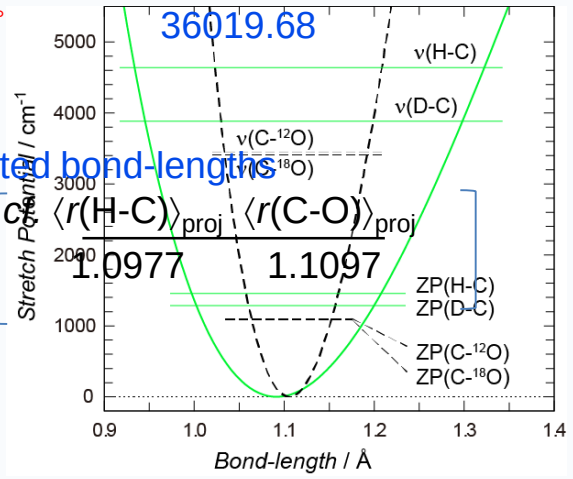
Exp. Amano *et al.*, *JMS* (2008)

	B_0 / MHz
H-^{12}C-^{16}O$^+$	44594.262(10)
H-^{13}C-^{16}O$^+$	43377.165(25)
H-^{12}C-^{18}O$^+$	42581.079(25)
D-^{12}C-^{16}O$^+$	36019.677(20)
D-^{13}C-^{16}O$^+$	35366.607(20)
D-^{12}C-^{18}O$^+$	34413.697(20)

$\langle\bar{\rho}\rangle_0 = 0$ is assumed → projected bond-lengths

r(H-C)	r(C-O)
1.0978	1.1068

r(D-C)	r(C-O)
1.0992	1.1064



cf.	$\langle r$(H-C)$\rangle_{proj}$	$\langle r$(C-O)$\rangle_{proj}$
	1.0977	1.1097

	Surfit		DVR3D (term value)		DVR3D Expectation value				
	B_0/MHz	%error	B_0/MHz	%error	$\langle r$(H-C)$\rangle_0$	$\langle r$(C-O)$\rangle_0$	$\langle\bar{\rho}\rangle_0$ ($\delta\rho$)	$\langle(B+C)/2\rangle$	%deviation
H-^{12}C-^{16}O$^+$	44588.3	-0.014	44594.6	0.0003	1.1121	1.1103	10.98 (5.6)	44527.2	-0.15
H-^{13}C-^{16}O$^+$	43371.3	-0.014	43377.4	0.0006	1.1120	1.1102	10.93 (5.6)	43312.9	-0.15
H-^{12}C-^{18}O$^+$	42575.3	-0.014	42581.3	0.0004	1.1121	1.1102	10.97 (5.6)	42519.5	-0.15
D-^{12}C-^{16}O$^+$	36016.8	-0.008	36021.9	0.0063	1.1065	1.1102	9.86 (4.9)	35968.0	-0.14
D-^{13}C-^{16}O$^+$	35363.8	-0.008	35368.6	0.0057	1.1065	1.1101	9.79 (4.9)	35315.8	-0.14
D-^{12}C-^{18}O$^+$	34410.9	-0.008	34415.6	0.0054	1.1065	1.1101	9.85 (4.9)	34366.1	-0.14

Units: B_0 (MHz), Distance (Å), Angle (degrees). r_e(H-C) = 1.0915 Å, r_e(C-O) = 1.1057 Å

$^1\Sigma^+$ HCN

Exp. Winnewisser et. al, *JMS* (1971)

	B_0 / MHz
H-^{12}C-^{14}N	44315.9755(4)
H-^{13}C-^{14}N	43170.08(6)
H-^{12}C-^{15}N	43027.69(5)
D-^{12}C-^{14}N	36207.4627(2)
D-^{13}C-^{14}N	35587.62(5)
D-^{12}C-^{15}N	35169.85(5)

From three Exp. B_0 values

3 roots for 3 B_0's

r(H-C)	r(C-N)	$\bar{\rho}$	→	B_0 (for H-^{12}C-^{14}N)
1.0892	1.1556	14.34°		44315.98

r(D-C)	r(C-N)	$\bar{\rho}$	→	B_0 (for D-^{12}C-^{14})
1.0790	1.1554	11.63°		36207.46

$\langle\bar{\rho}\rangle_0 = 0$ is assumed → projected bond-lengths

r(H-C)	r(C-N)
1.0673	1.1559

r(D-C)	r(C-N)
1.0660	1.1556

cf.

$\langle r$(H-C)$\rangle_{proj}$	$\langle r$(C-N)$\rangle_{proj}$
1.0627	1.1585

	Surfit		DVR3D (term value)		DVR3D Expectation value				
	B_0/MHz	%error	B_0/MHz	%error	$\langle r$(H-C)$\rangle_0$	$\langle r$(C-N)$\rangle_0$	$\langle\bar{\rho}\rangle_0$ ($\delta\rho$)	$\langle(B+C)/2\rangle$	%deviation
H-^{12}C-^{14}N	44289.4	-0.060	44290.6	-0.057	1.0798	1.1591	12.04 (6.2)	44133.5	-0.25
H-^{13}C-^{14}N	43143.4	-0.062	43144.5	-0.059	1.0798	1.1590	11.98 (6.2)	42993.6	-0.25
H-^{12}C-^{15}N	43001.4	-0.061	43002.7	-0.058	1.0797	1.1590	12.03 (6.2)	42853.0	-0.25
D-^{12}C-^{14}N	36193.1	-0.040	36194.1	-0.037	1.0755	1.1586	10.77 (5.5)	36072.6	-0.21
D-^{13}C-^{14}N	35572.8	-0.042	35573.7	-0.039	1.0755	1.1587	10.69 (5.5)	35455.1	-0.21
D-^{12}C-^{15}N	35155.4	-0.041	35156.3	-0.038	1.0755	1.1588	10.76 (5.5)	35040.6	-0.21

Units: B_0 (MHz), Distance (Å), Angle (degrees). r_e(H-C) = 1.0644 Å, r_e(C-N) = 1.1539 Å

Misbehaving results were obtained with $\langle\bar{\rho}\rangle = 0$: for r_0 structure determined from two B_0's.

$B_0 \rightarrow r_0$ Winnewisser *et al*. (Tab. 1 Winnewisser et al, *J. Mol. Spec*., **39**, 149 (1971))

	HCN	$H^{13}CN$	$HC^{15}N$	DCN	$D^{13}CN$
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$DC^{15}N$	1.061930(8) 1.156920(2)	1.062256(13) 1.156810(4)	1.062327(13) 1.156786(4)	1.07249(16) 1.15335(6)	1.05837(36) 1.15812(12)

$\Longrightarrow$ Δr
Black: r(H(D)-C) 0.01 Å
Blue: r(C≡N) 0.002 Å

Born-Oppenheimer approximation does not hold ? No!

Shrinkage parameter? NO !

They could not find the answer !

$\Longrightarrow$ Simply treat $\langle\bar{\rho}\rangle$ as a variable!

$^1\Sigma^+$ C_3

Exp. Giesen et al., *JCP* (2016)

	B_0 / cm^{-1}
^{12}C-^{12}C-^{12}C	0.43059156 (480)
^{12}C-^{13}C-^{12}C	0.43028231 (994)
^{13}C-^{12}C-^{12}C	0.41373380 (737)
^{13}C-^{12}C-^{13}C	0.39730106 (183)
^{13}C-^{13}C-^{12}C	0.41352775 (237)
^{13}C-^{13}C-^{13}C	0.39705749 (304)

Least-Squares Fit (LSQ) of Exp. B_0 values

3 roots for 6 B_0's

Residue	r(C1-C2)	r(C2-C3)	$\bar{\rho}$	→ B_0 (for ^{12}C-^{12}C-^{12}C)
6 x10^{-8}	1.2981	1.2981	22.46°	0.43044

$\langle\bar{\rho}\rangle_0 = 0$ is assumed → projected bond-lengths

Residue	r(C1-C2)	r(C2-C3)	*cf.* $\langle r(\text{C1-C2})\rangle_{proj}$	$\langle r(\text{C2-C3})\rangle_{proj}$
12 x10^{-8}	1.2774	1.2774	1.2759	1.2759

	DVR3D (term value)		DVR3D Expectation value				
	B_0 / cm^{-1}	%error	$\langle r(\text{C1-C2})\rangle_0$	$\langle r(\text{C2-C3})\rangle_0$	$\langle\bar{\rho}\rangle_0$ ($\delta\rho$)	$\langle(B+C)/2\rangle$	%deviation
^{12}C-^{12}C-^{12}C	0.42970	-0.207	1.2998	1.2998	19.69 (4.9)	0.42936	-0.287
^{12}C-^{13}C-^{12}C	0.42944	-0.195	1.2997	1.2997	19.56 (4.9)	0.42909	-0.277
^{13}C-^{12}C-^{12}C	0.41288	-0.207	1.2997	1.2998	19.60 (4.9)	0.41256	-0.284
^{13}C-^{12}C-^{13}C	0.39649	-0.204	1.2997	1.2997	19.51 (4.9)	0.39620	-0.278
^{13}C-^{13}C-^{12}C	0.41262	-0.219	1.2996	1.2997	19.47 (4.9)	0.41230	-0.298
^{13}C-^{13}C-^{13}C	0.39626	-0.201	1.2996	1.2996	19.38 (4.9)	0.39596	-0.277

Units: B_0 (cm^{-1}), Distance (Å), Angle (degrees). r_e(C-C) = 1.2944 Å

$^2\Pi$ NCS

Exp. Maeda *et al*., *Mol. Phys*. (2007)

	B_0 / MHz
$NC^{32}S$	6106.6230(16)
$NC^{34}S$	5962.857(52)

Least-Squares Fit (LSQ) of Exp. B_0 values

3 roots for 2 B_0's

Residue	r(N-C)	r(C-S)	$\bar{\rho}$	→ B_0 (for $NC^{32}S$)
8 x10^{-13}	1.1836	1.6345	7.77°	6106.64

$\langle\bar{\rho}\rangle_0 = 0$ is assumed → projected bond-lengths.

Residue	r(N-C)	r(C-S)	*cf.* $\langle r(\text{N-C})\rangle_{proj}$	$\langle r(\text{C-}^{32}\text{S})\rangle_{proj}$
79 x10^{-13}	1.1786	1.6336	1.1784	1.6333

	Surfit		DVR3D (term value)		DVR3D Expectation value				
	B_0/MHz	%error	B_0/MHz	%error	$\langle r(\text{N-C})\rangle_0$	$\langle r(\text{C-S})\rangle_0$	$\langle\bar{\rho}\rangle_0$ ($\delta\rho$)	$\langle(B+C)/2\rangle$	%deviation
$NC^{32}S$	6105.5	-0.018	6109.4	0.05	1.1836	1.6356	7.78 (1.9)	6109.39	-0.05
$NC^{34}S$	5961.9	-0.017	5965.8	0.05	1.1837	1.6355	7.78 (2.0)	5965.80	-0.05

Units: B_0 (MHz), Distance (Å), Angle (degrees). r_e(N-C) = 1.1778 Å, r_e(C-S) = 1..6335 Å

Similarlly for other molecules, $\bar{\rho}$ is determinde as,

Molecule	LSQ-Fit $\bar{\rho}_0$ /deg.	DVR3D Expect. value $\langle\bar{\rho}\rangle_0$ /deg.
$^3\Sigma^-$ FeCO	9.5	7.4
$^2\Pi$ NCS	7.8	7.8
$^1\Sigma^+$ HCO^+	12.5	11.0
$^1\Sigma^+$ DCO^+	9.8	9.8
$^1\Sigma^+$ HCN	14.3	12.0
$^1\Sigma^+$ DCN	11.6	10.7
$^1\Sigma^+$ C_3	22.5	19.7
$^1\Sigma^+$ CO_2	8.8	6.7

Good agreement between
LSQ fit and $\langle\bar{\rho}\rangle_0$.

⟹ Conventional belief, $\langle\bar{\rho}\rangle = 0$, for linear molecule is proved to be incorrect !!!

⟹ $\bar{\rho}_0$ should be treated as a variable.

Conclusions

Theoretically and experimentally,
ro-vibrationally averaged structure of a linear molecule is to be observed as being bent.

$\bar{\rho}_0 = 0$ yields bond-length projected onto *a*-axis. (r_s-structure also).
⟹ Without accompanied projection angle,
the value has no physical meaning as a structure parameter !!!

The r_0- (r_s-) data have been accumulated over more than half a century.
However, among them,
we never find any r_0- (r_s-) data accompanied by the projection angle !!!!!

What will happen ???? A remedy ? Yes, treat $\bar{\rho}_0$ as a variable !

Are Linear Molecules Really Linear ?

No: Theoretically (as Expectation value) and experimentally (in B_0 values), ro-vibrationally averaged structure of a linear molecule is observed as being bent.

Paradigm shift from $\bar{\rho}_0 = 0$ to $\bar{\rho}_0 > 0$ is requested.

In the interpretation of B_0 values, treat $\bar{\rho}_0$ as a variable !!!

Thanks to,

Koichi M. Yamada (AIST)
Keiichi Tanaka (Kyusyu Univ.)
Kensuke Harada (Kyusyu Univ.)
Kentaro Kawaguchi (Okayama Univ.)

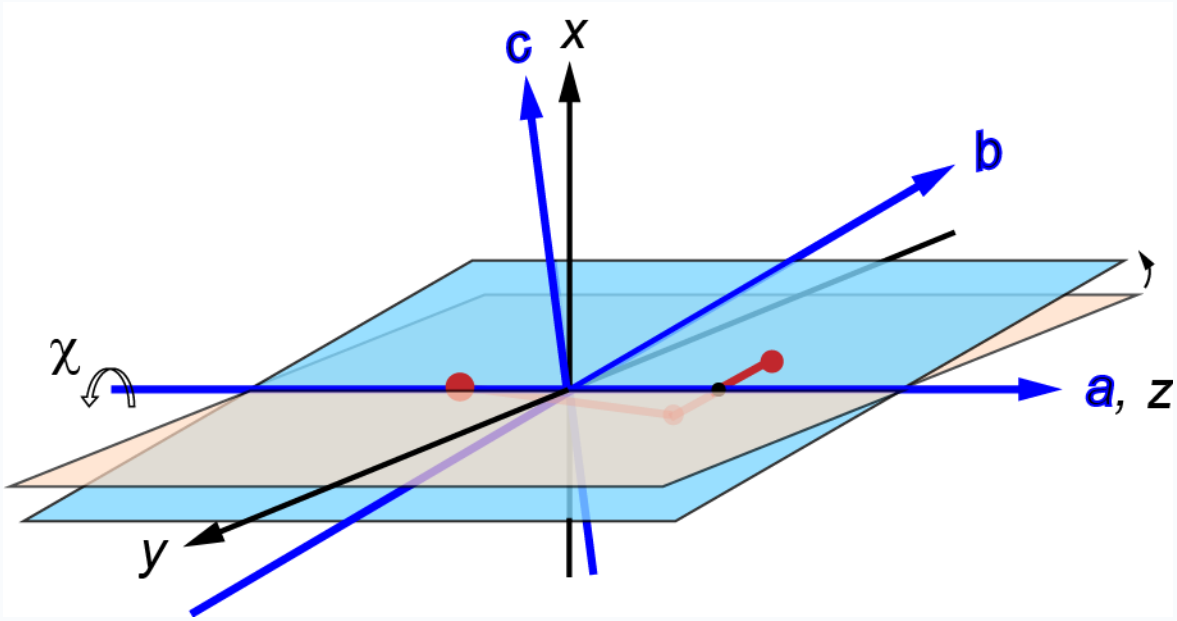
And, especially to,
An anonymous Professor (?? Univ.)

E pur la terra si muove !

In the case of linear molecule, always $(B+C)/2$ is observed due to the double degeneracy.

Even $\langle\bar{\rho}\rangle_0 > 0$, rotational constants B and C are never observed as separate values.

Instantaneous bending plane



If rotation about the *a*-axis does not occur (*i.e.* if there is no double-degeneracy in the bending vibration), the spectrum pattern would become asymmetric top.

However, ….

To avoid misunderstanding;

What is the averaged zero-point structure of a linear molecule ??

Nature
(World of Schrödinger eq.)

ψ_{bend} is maximum at linear.

→ Average is a linear shape!

Observation ←

→ Results

We

$\langle \bar{\rho} \rangle_0$ (Theory)

Observed as being bent !!

Why? Because of double degeneracy of bending motion of a linear molecule.

E.g.: 1*s* orbital of H atom

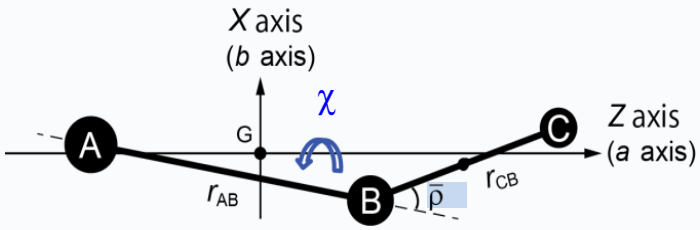
Max. on the nucleus

Theoretical observation ←

→

Electron Density:
Max. at Bohr radius.

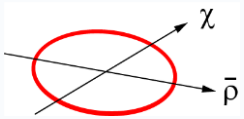
2D-Oscillator (Bending mode)



$\bar{\rho}$ is the supplement of the bond-angle (as x-axis),
χ is the rotation angle about a-axis (as y-axis)

Bending wavefunction: a Laguerre-Gauss wavefunction (Boháček, *CPL*, 1976)

$$\varphi_{v,\ell}(\bar{\rho},\chi) = N \exp(i\ell\chi)\, \phi_{v,\ell}(\bar{\rho}), \qquad (0 \le \chi \le 2\pi,\ 0 \le \bar{\rho} < \pi). \qquad (1)$$



Normalization of eq. (1),

$$\begin{aligned}
\langle \varphi_{v,\ell}(\bar{\rho},\chi) | \varphi_{v,\ell}(\bar{\rho},\chi) \rangle &= \iint |\varphi_{v,\ell}(\bar{\rho},\chi)|^2\, \bar{\rho}\, d\bar{\rho}\, d\chi \qquad (2)\\
&= \int_0^{2\pi} |\exp(i\ell\chi)|^2\, d\chi \int_0^{\pi} N^2\, \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}\, d\bar{\rho}\\
&= \int_0^{\pi} 2\pi\, N^2\, \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}\ d\bar{\rho} = 1\,. \qquad (3)
\end{aligned}$$

Thus, we get renormalized wavefunction:

$$\Phi_{v,\ell}(\bar{\rho}) = \sqrt{2\pi} N\, \phi_{v,\ell}(\bar{\rho})\, \sqrt{\bar{\rho}}, \qquad (0 \le \bar{\rho} < \pi)\,.$$

Expectation value $\langle \bar{\rho} \rangle$ using eq. (1) or eq. (4):

$$\begin{aligned}
\langle \bar{\rho} \rangle &= \langle \varphi_{v,\ell}(\bar{\rho},\chi) | \bar{\rho} | \varphi_{v,\ell}(\bar{\rho},\chi) \rangle = \langle \Phi_{v,\ell}(\bar{\rho}) | \bar{\rho} | \Phi_{v,\ell}(\bar{\rho}) \rangle\\
&= 2\pi\, N^2 \int_0^{\pi} \phi_{v,\ell}(\bar{\rho})^2\, \bar{\rho}^{\,2}\ d\bar{\rho}\ .
\end{aligned}$$

Hence, for any bending states, $\langle \bar{\rho} \rangle > 0$.